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THE UNIVERSITY OF ALBERTA

"PYROLYSIS OF PROPANE IN AN AUTOTHERMIC REACTOR"

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES IN PARTIAL
FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER
OF SCIENCE

DEPARTMENT OF CHEMICAL ENGINEERING
BY
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ABSTRACT

A pilot plant furnace was built and operated to obtain performace data suitable for commercial evaluation and scale up, on the pyrolysis of propane to ethylene and acetylene. In the reactor a stream of preheated propane flowed down between two surface combustion burners from which flowed streams of hot combustion product gases. The reacting gases were rapidly quenched to arrest the pyrolysis before the products were decomposed into carbon and hydrogen.

After operating the furnace for some time it was realized that the flow arrangement gave very little mixing of the two streams. As a result the reaction had a great variety of compositions, temperatures and residence times in various zones in the reactor. Since only the overall off-gas analysis was available no interpretation or correlation of the data was attempted.

Qualitative interpretation of the reactor data was made by comparing it with data reported in the literature on other similar reactors. It was found that the reaction system would merely become a partial combustion system if the mixing could be done very rapidly; about 0.001 seconds. It was also determined that water was practically inert during the short residence time of the pyrolysis reaction while carbon dioxide reacted to form carbon monoxide at a rate equivalent to the pyrolysis.

It was concluded that this type of process could have advantages over partial combustion processes if hydrogen was the fuel and if a fast mixing reactor was developed.

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INTRODUCTION

The purpose of the experimental work outlined in this thesis was to investigate a pilot plant furnace for pyrolysing propane to acetylene and ethylene, with the main objective of obtaining engineering data useful in scaling up to a commercial size installation. Basically the furnace was to consist of two tunnel type surface combustion burners enclosed in a reaction chamber into which propane was to be fed. Within this reaction chamber, the hot combustion products from the burners mixed with the incoming propane and supplied the necessary energy to pyrolyse the propane. This furnace design eliminated the need for heat transfer from a heat source to the propane but the resulting mixture of pyrolysis products was diluted considerably by the combustion products and nitrogen from the burners.

CHEMICAL UTILIZATION OF ACETYLENE AND ETHYLENE

Of the primary materials used in manufacturing products generally classified as petrochemicals, ethylene is the most important. Plastics, insecticides, paints, explosives, medicinals and vitamins, gasoline additives and many more items may be produced from ethylene. At the present time, direct conversion of ethylene is dominated by the production of ethylene oxide, synthetic ethanol and polyethylene. These three compounds consume about 75 per cent of the total ethylene production, with ethylene oxide requiring the greater share, while the latter two consume approximately equal amounts.

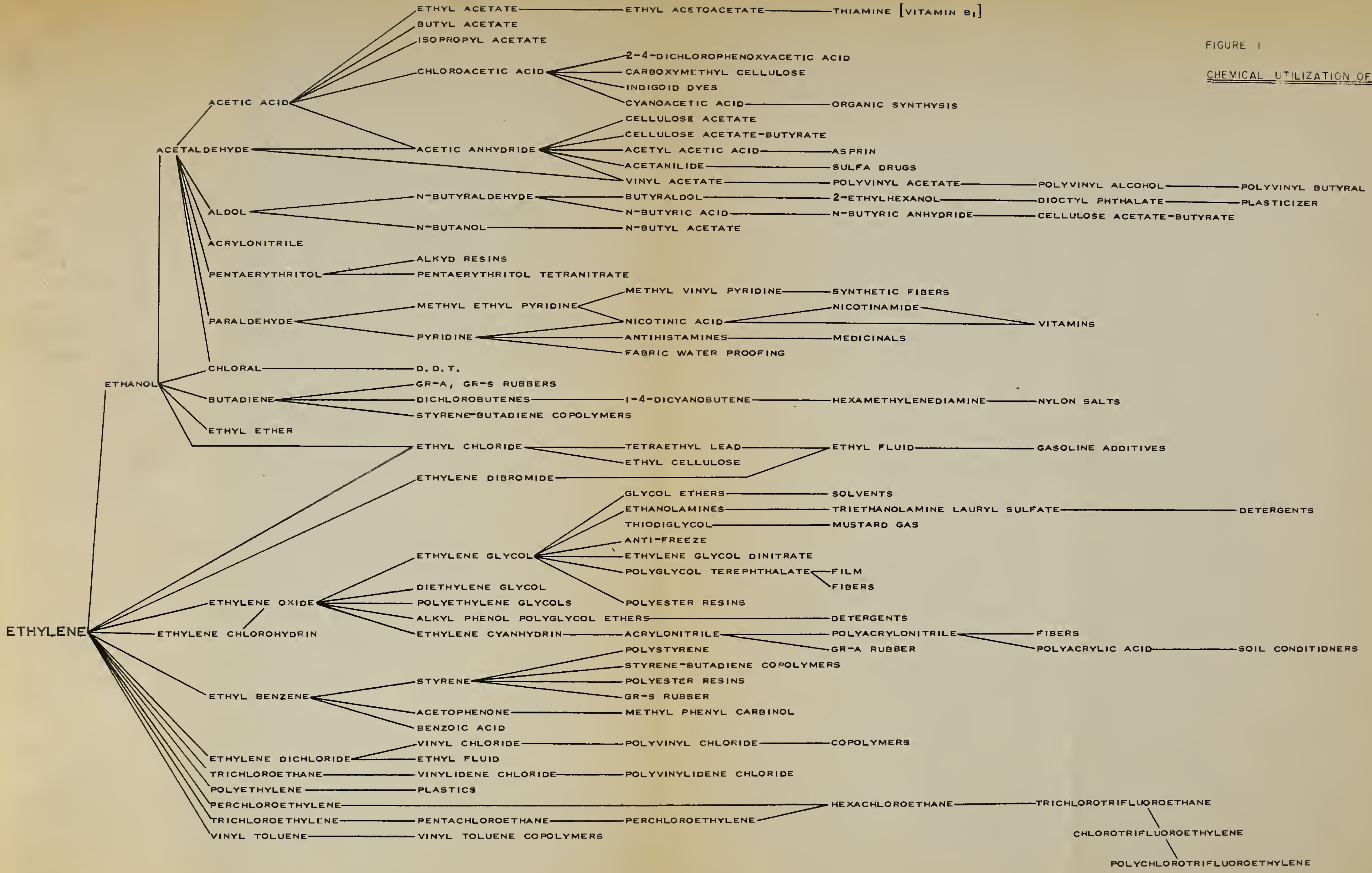
In the United States, the yearly ethylene production reached 3.9 million pounds in 1957. Since then, production has steadily increased with the forecasted production for 1965 set at 6.5 million pounds.(1)

Theoretically, any chemical compound produced from ethylene may also be manufactured from acetylene. However, it is a considerably more costly raw material than ethylene and is used only when it offers technical advantages. The production of acetylene is dominated by the carbide process. Up to 1954, acetylene production from sources other than calcium carbide has been estimated to be less than 10 per cent. Since then, the production of acetylene from petroleum hydrocarbons has increased in importance.

Theoretically any hydrocarbon is a possible source of acetylene or ethylene. The economics of production and availability of feed stock, however, determine the raw material used. For making ethylene, ethane is probably the best raw material. Propane, butane, naphthas, gas oil and several other hydrocarbons may be used. Similar feed stocks are used in the production of acetylene.

FIGURE I

CHEMICAL UTILIZATION OF ETHYLENE(2)



PRODUCTION OF ACETYLENE AND ETHYLENE

Tubular Reactor(3)

Tubular reactors are used commercially to produce ethylene and propylene by cracking a variety of feed stocks ranging from ethane and propane to naphtha, gas oil and other liquid petroleum fractions. In these reactors, the feed is cracked inside externally heated tubes. These tubes range in size up to about 4.5 inches in diameter, and are usually fabricated out of high chromium alloy steels capable of withstanding temperatures up to about 1800 °F. Alloys low in chromium and high in nickel are not suitable because of their tendency to promote carbon formation.

Operating variables possible are: reactor pressure; cracking temperature; and residence time. Outlet pressures of the tubes may range from 10 psig., for the heavier molecular weight feeds, to about 30 psig. for ethane and/or propane. The pressure drop through the furnace varies up to about 30 psi., depending upon through-put and tubing diameter. Normally, through-put is based on heat transfer considerations. High linear velocities are required to maintain the wall temperatures at a reasonable level by high heat transfer rates from the metal to the hydrocarbon being cracked. These high linear velocities are often attained at the expense of increasing pressure drop. Cracking temperatures range from about 1200 °F, for high molecular weight feeds, to 1500 °F for ethane. The temperature may be controlled to some extent by residence time and by control of the temperature of the flue gases leaving the furnace. Residence times range from about 0.3 to about 1.5 seconds.

Carbon deposition on the tube walls is often encountered. This causes a reduction in heat transfer rates and in some cases, if left unchecked, may plug off the tubes. Injection of steam with the feed stock is usually used to minimize carbon formation. Ethylene yields range from 75 per cent from ethane, 45 per cent from propane to about 25 per cent for the pyrolysis of naphthas.

Wulff Process(4,5)

The Wulff Process, used primarily to manufacture acetylene, utilizes a regenerative furnace to obtain the required high temperature. The furnace is constructed in the form of a box filled with refractory checkers of a special shape and material. One or two sections within the furnace are left open for use as combustion chambers.

Operation of the furnace is on a four-phase cycle. Air is forced into the furnace from one end, through hot checker bricks, and is preheated before it enters into a combustion chamber. In the combustion chamber, natural gas or other fuels are injected and burned. The combustion products leave through the other end of the furnace, heating up the remaining checker bricks. Hydrocarbon feed, diluted with steam in a ratio of about 1:6, is forced into the hot end of the furnace where it is cracked. The cracked products pass on through the colder checker work at the other end of the furnace, and into a quench tower. In the cold checker work, limited quenching is attained and some of the heat is recovered. Reversal of these two operations completes the cycle.

Feed stocks used may range from methane to liquid petroleum fractions such as gas oil. Operating temperatures range from 2650 °F for methane feed, 2300 °F for ethane, propane and butane, to slightly lower temperatures for the heavier feed stocks. Residence time within the furnace is in the order of 0.1 seconds, with yields of up to 50 per cent by weight conversion to ethylene and acetylene.

This process is not popular in North America, with the only plant in operation being a demonstration plant operated in Los Angeles by the Wulff Process Company.

Thermofor Pyrolytic Cracking(6,7)

This method of cracking petroleum hydrocarbons was developed, by the Socony-Vacuum Oil Company, to produce ethylene and aromatics from feed stocks ranging from ethane to reduced crudes. Heat required to preheat and crack the hydrocarbon is transferred to the gas by hot pebbles moving continuously through the reactor.

The major pieces of equipment required are: a heater for the pebbles; a reaction chamber; and some method of continuously circulating the pebbles through the reactor and the heater. Pebbles, recovered from the reactor at about 1000 °F, are heated to about 1600 °F by the direct combustion of fuel within the pebble bed. During this heating period, carbon deposits, formed on the pebbles in the reactor, are burned off. The heater is situated directly above the reactor to allow gravity feeding of the pebbles into the reactor. Within the reactor, the pebbles transfer heat to the cracking hydrocarbon at a rate of about 15,000 BTU/hr./°F/cubic foot of pebbles. This high heat transfer rate rapidly heats the feed stock to cracking temperature and minimizes undesirable low temperature reactions.

Temperatures within the reactor are controlled by adjustment of the depth of the pebble bed and the residence time of the hydrocarbon feed. Some control of temperature is also obtained by controlling the temperature of the pebbles leaving the heater.

Movement of the pebbles from the reactor to the heater is accomplished by means of a bucket elevator in the Socony-Vacuum process. A similar unit, developed by the Philips Petroleum Company, utilizes an air lift mechanism to raise the pebbles to the heater.

The pebbles used are a non-catalytic refractory and range from 0.2 to 0.4 inches in diameter. Physical properties that must be met by the refractory are: high density for compact design; high specific heat in order to reduce the weight of pebbles that must be circulated; high resistance to wear, spalling and breakage; low abrasion characteristics to minimize wear on the vessels; and a high softening temperature.

Yields attainable range from 55 per cent by conversion of ethane to ethylene, on a per pass basis, to 12 per cent conversion to ethylene using a light naphthene feed stock.

The Sachsse Process(8,9,10,11)

In the United States today, about twenty commercial plants use this process to produce acetylene from natural gas. The process is based on partial combustion of the feed to provide the heat necessary to pyrolyze the unburned hydrocarbon to acetylene. By this means, the high heat requirements are produced in intimate contact with the feed stock, eliminating the need for heat transfer. This advantage, however, is counterbalanced by the necessity of separating the acetylene from a more dilute off gas stream, and of providing a supply of commercially pure oxygen (95% pure). Natural gas, with a high methane content, is used primarily as the hydrocarbon feed.

The reactor (Fig. 2), consists of a mixing chamber, a burner block, a reaction flame zone, and a water quench chamber. Preheating the oxygen and methane separately to about 1200 °F reduces the amount of oxygen required to maintain temperatures above 2200 °F in the reaction zone, and increases the flame velocity, allowing higher throughput per unit of reactor. Iron and nickel are avoided in the hydrocarbon preheaters and the reactor since they promote the cracking of methane to carbon and hydrogen. Alloys, high in chromium and silicon, are used in the methane preheater tubes to reduce carbon

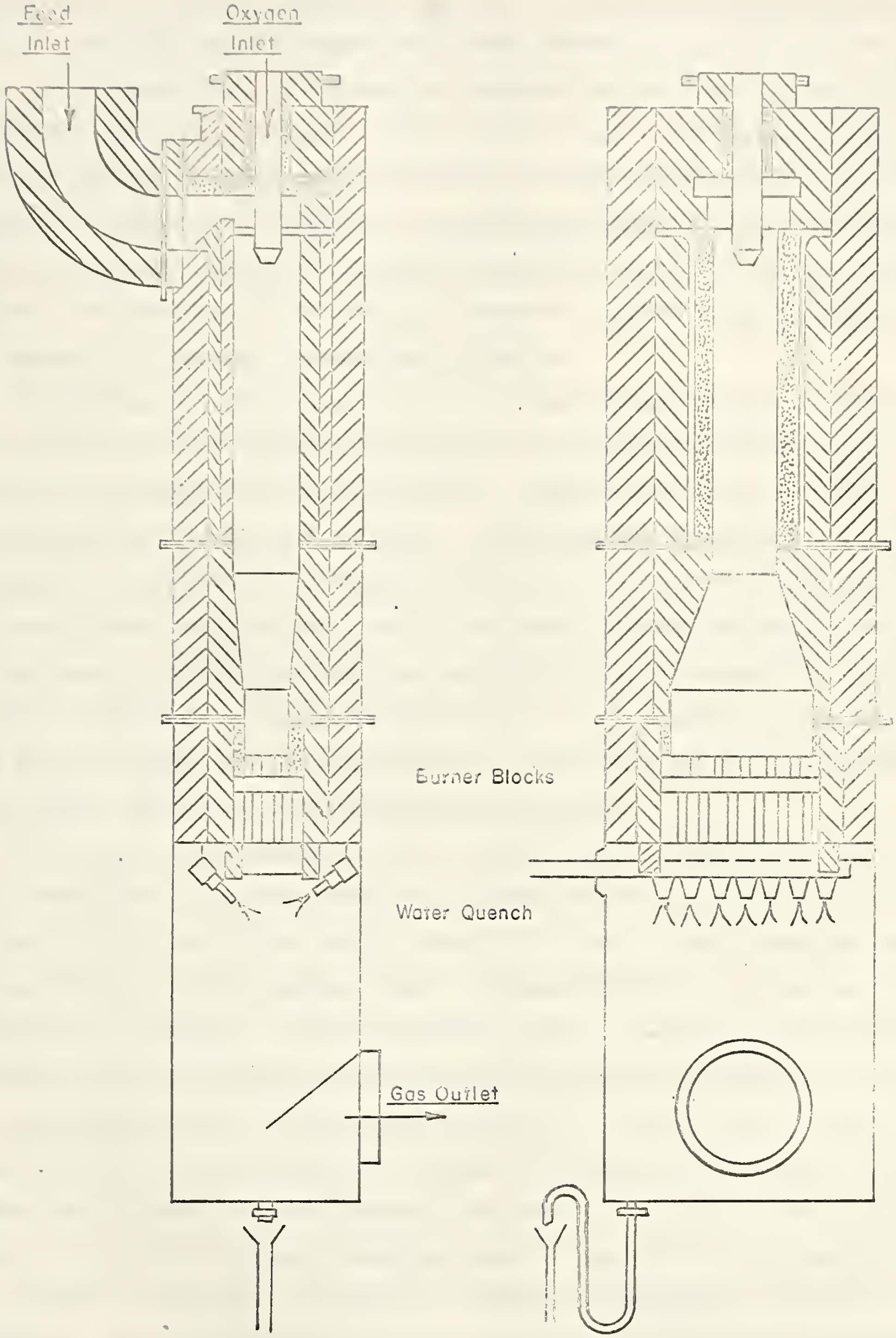


Figure 2. Acetylene Burner – Sachsse Process

formation, and velocities in the order of 500 feet per second are maintained to eliminate deposition of any carbon formed. Oxygen is preheated in nickel alloy tubes.

During the brief induction period of the combustion reaction, the oxygen and feed are thoroughly mixed and blown through the burner block into the flame zone. To insure that no explosive mixture in the mixing zone will have sufficient residence time to ignite, and to give complete mixing, the inlet velocity of the methane is maintained at about three times the velocity of the oxygen. In addition, oxygen is introduced tangentially, utilizing centrifugal force to keep an oxygen rich, non-combustible mixture in the boundary layer on the wall of the mixer. Since this layer will have a zero average velocity, any explosive mixture present would ignite.

Flash-back of the flame into the mixer is prevented by the small diameter of the holes in the burner block which, in addition, acts as an insulator between the flame zone and the mixer. Additional mixing in the burner blocks is attained by having two sections, separated by an open space, with the holes staggered. Impurities in the natural gas such as hydrogen, carbon monoxide, and unsaturates must be avoided since these substances will react faster than the methane, causing preignition and failure of the reactor. Thus, any preliminary cracking in the preheaters must be eliminated. One problem not overcome by the design is the elimination of dusts from the feed gases, especially rust, which catalyses the combustion reaction.

The geometrical design of the burner block stabilizes the flame by creating high turbulence and associated high flame velocities due to the convective mixing of hot reacted gas with fresh inlet gas. Upon reaching the flame zone, the uniformly premixed gases react independently of the mixing speed, making it possible to apply a short residence time, less than 0.01 seconds, to all of the acetylene formed, thus minimizing extreme cracking to carbon and hydrogen.

Quenching of the reaction is attained by water sprays which provide a large surface area of fine water drops having enough force to penetrate the entire gas stream. Gases leaving the reactor at 180 $^{\circ}$F are saturated with water vapor. A typical off-gas contains about 9 per cent (dry basis) acetylene.

About 5 per cent of the gas charged is completely cracked to carbon and hydrogen. The soot carried in the reactor gas is removed by counter-current contacting with a moving bed of pulverized coal. Some carbon builds up within the reactor and periodic cleaning is required.

A typical commercial operation requires 5.6 tons of commercial oxygen and 193 MCF of natural gas to produce one ton of acetylene.

Cracking of Feed Stocks by Mixing With Hot Combustion Gases(12,13)

Several processes have been developed based on the separate burning of a fuel and subsequent mixing of the hot combustion products with a feed stock. Variations in this type of process lie primarily in the construction of the burners and in the methods and types of equipment used to mix the gases.

Both liquid and gaseous fuels may be used with either air or oxygen to support combustion. The use of air results in lower temperatures, giving less tar and carbon formation, but also increases separation problems caused by nitrogen dilution of the desired products.

Combustion may be separated completely from the feed stock, or as in one design, combustion may occur in the same section into which the feed is introduced. This particular design employs a cylindrical, refractory lined reactor into which the feed stock enters axially to be thoroughly mixed with the combustion products. Other designs utilize a combustion chamber in which the fuel is burned in ceramic or in water cooled, metal burners. In these units the feed stocks are mixed with the combustion products before entering a reaction chamber.

Feed stocks used range from ethane to liquid petroleum fractions for production of ethylene and/or acetylene. Methane may be used to produce acetylene.

Temperatures developed within the burners may run as high as 2000 °C. Variations in operating conditions of the burner-reactor units, by varying amounts of fuel and feed and the ratio of fuel to feed, will alter acetylene to ethylene ratios over a range of from 0.3:1 to 4:1. Conversions of up to 56 weight per cent ethylene plus acetylene are obtainable. Reaction times are in the order of 0.001 seconds.

One such process has been developed by the Tennessee Eastman Company of Kingsport, Tennessee. A research program was undertaken to develop a process to produce acetylene from saturated hydrocarbons, with yields comparable to or higher than existing processes. Other basic aims of the program were:

i. to eliminate cyclic operation of the regenerative furnace (Wulff Process);

ii. to eliminate the high electrical energy requirements of the arc process;

iii. and to eliminate or reduce the relatively high oxygen requirements of the partial combustion processes (eg. Sachsse).

The furnace, developed and used on a pilot plant scale, consisted of a combustion chamber, a mixing zone, and a reaction chamber. These three sections were circular in cross-section and had a common horizontal axis. Air, or oxygen, and natural gas entered the combustion chamber through an annular mixer. The products of combustion left the chamber and entered a restricted mixing zone leading to the reaction chamber. A hydrocarbon feed was introduced into the combustion products at the inlet to the mixing zone. Within this zone, the relatively high velocity and turbulence completely mixed the gases before their entry into the reaction chamber. The feed started dissociating in the mixing zone and the reactions forming the unsaturated products were completed in the reaction chamber. The gas mixture was then quenched, by a direct water spray, to stabilize the reaction products.

Experimental work was conducted for approximately one year, during which time both oxygen and air were used to support combustion of the natural gas fuel. Data were obtained on the cracking of propane, using both air and oxygen supported combustion, and on cracking of a natural gasoline, using air supported combustion. Reaction temperatures were controlled by the amounts of combustion gases and feed stock used in conjunction with variations in preheating of the streams. The reaction time was varied by changing the amount of material put through the unit. Steam dilution of the feed stock, and addition of steam to the air or oxygen was used to control the formation of carbon and tars.

Experimental work done indicated a conversion of 56 weight per cent of propane to acetylene and ethylene. Conversions of 45 weight per cent to acetylene alone were obtained with a slight drop in total conversion. Approximately equal conversions were attainable using both oxygen and air supported combustion. With oxygen, the amount required per pound of product was found to be less than that reported for other processes.

The amounts of carbon and tar formed were found to depend upon the amount of steam fed into the furnace. At high temperatures and prolonged residence times the amounts of these products formed were increased. However, they were effectively controlled by steam addition. More steam was used with oxygen than with air, resulting in less tar formation.

Comparision of the results obtained with propane and natural gasoline showed that slightly higher yields were obtained with natural gasoline at low acetylene to ethylene ratios. With more severe cracking, to produce high

acetylene to ethylene ratios, slightly higher yields were obtained using propane feed. Natural gasoline produced more tar than propane at the same conditions, requiring the use of more steam when feeding natural gasoline. A comparison of fuel requirements showed that about 10 per cent more per pound of product was required with natural gasoline. This increased requirement was attributed to the larger amounts of diluent steam required.

Aromatics and higher acetylenes were produced in varying amounts. Slightly higher amounts were produced when using oxygen supported combustion.

In a commercial operation using this process, the choice of feed stock and choice of air or oxygen to support combustion would be based on economic factors. The availability and cost of light hydrocarbons would dictate the feed stock used since all of the lighter hydrocarbons should be suitable as a feed. In choosing air or oxygen, the economics of added facilities required to produce pure oxygen would have to be weighed against added recovery and processing facilities dictated by nitrogen dilution resulting from the use of air.

Surface Combustion Reactor(14)

Under the sponsorship of the Research Council of Alberta, a process, similar to the last commercial design described, has been investigated. Two experimental furnaces have been built and operated at the University of Alberta.

The design of the furnaces constructed, centered around the use of surface combustion burners as a heat source. These burners were mounted inside a refractory lined steel shell. Within the furnaces, open spaces existed in which a feed stock and combustion products from the burners were mixed. The heat required to pyrolyse the feed stock was generated immediately within the reaction zone, in direct contact with the feed. This design eliminated the need of heat transfer from some outside source. However, one serious drawback present was the dilution of the pyrolysis products with carbon monoxide, carbon dioxide and nitrogen from the burners.

Surface combustion involves rapid and complete combustion of an explosive gas mixture with a minimum amount of flame. Such a phenomenon occurs at the surface of an incandescent solid. Several types of burners using this principle have been developed. Essentially these burners consist of a shell, into which the combustible mixture is introduced, faced with a burner block. The variation in burners is primarily a variation of the type of burner block used.

One common type of burner utilizes a porous refractory plate through which the fuel mixture is forced. Combustion occurs within the interstices of the plate. Similar to this, are burners with a block of non-porous material containing holes or tunnels. The shape and diameter of these tunnels may vary, with some burners having tunnels of constant diameter, whereas others have small diameter inlets with larger diameter outlets. With these burners, the combustion occurs within the tunnels. Another variation in burner design utilizes a drilled non-porous refractory plate through which the fuel mixture passes to impinge upon refractory surfaces. The combustion reaction takes place on the impinged surfaces.

Many of the burners used commercially have the surfaces, on which combustion occurs, coated with a catalyst to promote complete combustion. These burners operate efficiently at temperatures as low as 1400 $^{\circ}$F. Burners not coated with a catalyst are, in general, unstable at the lower temperatures, requiring a surface temperature of about 2000 $^{\circ}$F or higher for complete combustion.

Prior to the construction of the first furnace, several types of burners were tested. Both the porous plate and tunnel type burners showed possibilities for use in pyrolysis furnaces.

The first furnace constructed was designed and operated by J.W. Slupsky (M. Sc. Thesis, 1958). This furnace contained one surface combustion burner with a reaction zone measuring 11.625 x 11.625 x 1.625 inches. The burner (manufactured by Radiant Heating of London, England) consisted of a porous refractory plate, 11.625 inches square by 1.5 inches thick, mounted in a cast iron shell. With an operating range of 1200 $^{\circ}$F to 1500 $^{\circ}$F, the maximum heat release of the burner was 50 M-BTU/sq. ft.(hr.).

A premixed stoichiometric stream of air and natural gas was fed to the burner, and propane feed stock was introduced perpendicular to the flow of combustion products.

Tests run, were conducted at three different fuel rates, ranging from 0.45 SCFM to 1.16 SCFM. With each fuel rate, the ratio of fuel to feed was varied from about 3.0 to 6.0. The off-gas stream was analysed by gas chromatography.

During the operation of this furnace, it was found that the introduction of propane had no appreciable effect on the combustion. However, flash-back was encountered when the burner surface exceeded 1800 $^{\circ}$F.

In order to evaluate mixing within the furnace, Reynolds Numbers were calculated and found to range from 150 to 1500. This would indicate little or no mixing attained from turbulence. However, since the feed was introduced at right angles to the flow of combustion products, it was felt that a reasonable amount of mixing was obtained.

Data obtained with the furnace indicated a product distribution similar to that obtained in commercial installations. Thermal efficiencies obtained where rather low, ranging from a low of 40 per cent to a maximum of 70 per cent.

The design, construction and operation of a second furnace using surface combustion burners lead to the presentation of this thesis.

THERMODYNAMICS

Thermodynamics cannot indicate reaction rates or possible reaction mechanisms. It can, however, serve as a means of predicting driving forces and the effects of temperature, pressure and ratio of reactants through calculation of equilibrium conversion to products.

Equilibrium yields calculated from thermodynamic data set the asymptotic limit to which a conversion may approach but never exceed. In the pyrolysis of hydrocarbons at high temperatures, the favored equilibrium is complete decomposition to form hydrogen and carbon. Since carbon formation is minimized by establishing operating conditions to favor the formation of some desired product, such as ethylene or acetylene, equilibrium conversions may be calculated under the assumed condition of no carbon formation, or an arbitrarily set amount of carbon being formed. The pyrolysis reactions are generally carried out at high temperatures and relatively low pressures (about 1 to 3 atmospheres); conditions at which most of the gaseous products and reactants may be assumed to behave as ideal gases. With this assumption:

$$-\Delta F^{o} = RT(\ln Kp).$$

Where: ΔF^{o} = the change in free energy at the standard state occurring with the reaction;

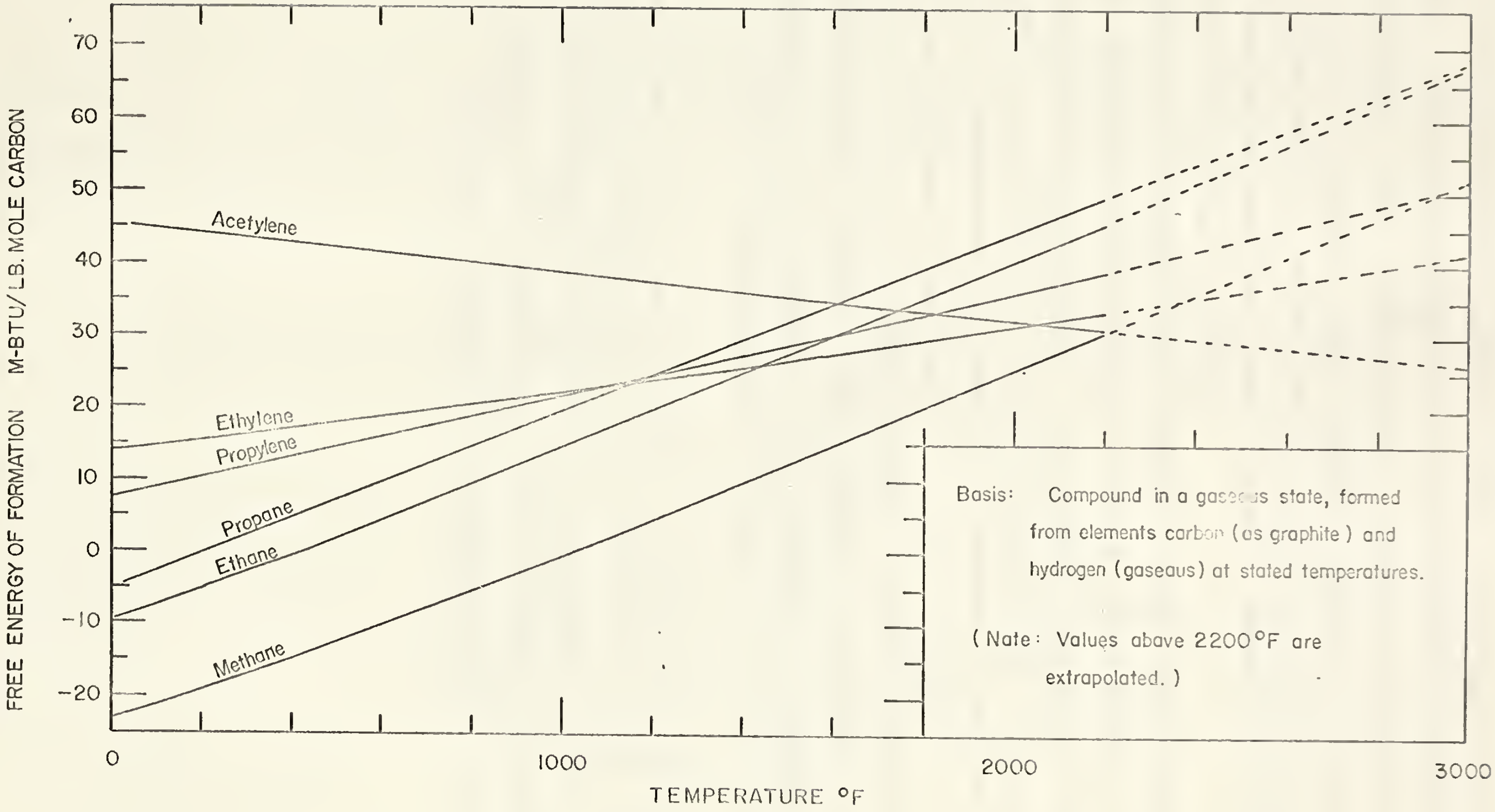
R = gas constant;

T = absolute temperature at which the reaction occurs;

Kp = equilibrium ratio.

In a system where one or two reactions occur, the calculation of the equilibrium concentrations is relatively simple. However, in a system with several reactions of both reactants and primary products possible, calculation of the equilibrium concentrations can become very complicated and time consuming. The pyrolysis of propane involves numerous reactions to produce hydrogen, saturated hydrocarbons, olefins, and acetylenes. For this reason, no attempt has been made here to calculate specific equilibrium yields.

Without calculating equilibrium yields, it is possible to qualitatively determine conditions favoring a reaction. From the equation relating equilibrium constant and free energy change, a given set of conditions may be evaluated as to whether or not they favor a desired reaction. At temperatures where the free energy change is positive, the equilibrium constant will be less than 1.0, indicating a driving force favoring retention of the reactants.



Basis: Compound in a gaseous state, formed from elements carbon (as graphite) and hydrogen (gaseous) at stated temperatures.

(Note: Values above 2200°F are extrapolated.)

Figure 3 Free Energies of Formation[15]

Negative free energy changes give equilibrium constants larger than 1.0 and indicate driving forces favoring product formation.

At conditions where the driving force starts to favor the formation of desired products, substantial amounts may not be formed since reaction rates may not be significant. This is shown by the conversion of propane to ethylene and methane. At 625 °F, the free energy change indicates a driving force favoring the desired reaction, but the reaction rate is negligible; in the order of 10^{-10} recriprocal seconds. Thus, negligible amounts of ethylene and methane are formed from propane at 625 °F.

Such conditions are in many cases, desirable, since they allow preheating of reactants to temperatures where driving forces do exist without the danger of reactions starting during preheating. This makes it possible to supply much of the required sensible heat to the reactants outside the reactor.

An increase in temperature will produce an increase in reaction rate and, for many reactions, increase the driving force. This increase in driving force may not, however, show up as an increase in yield. At the elevated temperature additional reactions may be favored. These reactions may consume either the products or reactants. This is evident in the pyrolysis of propane to ethylene. At approximately 2200 °F the decomposition of ethylene to acetylene becomes significant.

Thermodynamics may also be used to predict the heat load required for a reaction at some specified temperature. In the pyrolysis of light hydrocarbons, the total heat load calculated can only be an approximation to actual conditions. The reactions occurring do not proceed in a clear cut manner and numerous side reactions occur. This makes it impossible to calculate exactly the amount of heat required.

PYROLYSIS MECHANISM

The mechanism originally proposed for hydrocarbon pyrolysis was the splitting of a molecule with the simultaneous shift of hydrogen atoms to produce an olefin and a short chain saturated hydrocarbon and hydrogen. Another proposed mechanism assumed the breaking of the terminal C-C bond accompanied by the formation of methane. Still another mechanism proposed the formation of $-CH_3$, $=CH_2$, and $\equiv CH$ particles. Rice (16), however, assumed only the formation of methyl, ethyl, propyl, and comparable heavier radicals in the breakdown of a hydrocarbon. Today, only the molecular rearrangement and the free radical mechanism proposed by Rice are accepted.

In the pyrolysis of propane the primary products are ethylene and methane, and propylene and hydrogen according to the reactions:

$$C_3H_8 \longrightarrow C_2H_4 + CH_4$$

$$C_3H_8 \longrightarrow C_3H_6 + H_2$$

The formation of propylene may be explained by the splitting out of a hydrogen molecule formed from hydrogen atoms removed from two adjacent carbon atoms. A similar explanation for the formation of ethylene would require a hydrogen atom to jump from a 1 position to a 3 position to split out methane. Alternative to this, would be the removal of a methyl group and a hydrogen atom from the adjacent carbon to form methane, followed by the rearrangement of the ethylidene radical to form ethylene.

Rice proposed that these mechanisms were improbable and that similar mechanisms would become even more improbable and more complicated in explaining the pyrolysis of higher molecular weight alkanes. For this reason, Rice felt that the decomposition mechanism could be best explained by the use of the free radical concept.

In the pyrolysis of a saturated hydrocarbon, primary decomposition of a molecule occurs by the splitting of either a C-C bond or a C-H bond. Prediction of this split would be possible with an estimation of bond strengths. From various measurements (17), the average bond strengths have been estimated at 98.2 kcal./g-mole for C-H, and 80 kcal./g-mole for C-C. This would indicate that the favored reaction, requiring less energy, would be the breaking of a C-C bond.

A methyl free radical produced in this manner, could undergo two possible

reactions:

i. removal of a hydrogen atom from a paraffin molecule, forming a new free radical;

ii. or combination with another free radical to form a saturated hydrocarbon.

The latter reaction would tend to end the possibility of a chain of reactions, whereas the former would produce another free radical to sustain this chain.

The free radicals formed by the removal of a hydrogen from a saturated molecule would undergo one of two chain sustaining reactions. They may remove hydrogen atoms from other paraffin molecules, reforming the original molecule and producing new free radicals, or they may form an olefin by ejecting a hydrogen free radical. A third possible reaction would be the combination with another free radical and formation of a saturated hydrocarbon.

When a free radical attacks a saturated hydrocarbon molecule to remove a hydrogen atom, the choice of hydrogen removed will depend to some extent upon bond strengths and the number of hydrogens available. Thus, in a molecule containing tertiary, secondary and primary hydrogens, the choice would favor the removal of the more loosely held tertiary hydrogen. In a straight chain molecule, with only primary and secondary hydrogen atoms, the probable choice would be a secondary atom. In opposition to this choice, however, is the availability of the various hydrogens. Methane and ethane contain only primary hydrogens (although the hydrogen atoms in ethane are more loosely held than those in methane) whereas propane contains a ratio of 6 primary atoms to 2 secondary hydrogen atoms. Thus, in the pyrolysis of propane the chances of removing a primary hydrogen are three times that of removing a secondary. This availability of the primary atoms decreases with increasing molecular weight, making the chance of selection of a secondary hydrogen greater. A similar condition would prevail for the availability and selection of a tertiary hydrogen from a branched molecule.

Basis for accepting the molecular rearrangement mechanism may be explained by work done on the pyrolysis of ethane.(17) Addition of small amounts of NO_2 were found to decrease the rate of decomposition due to its inhibiting effect on free radicals. Increased addition of NO_2 cut the reaction rate to a limiting value of about 8 per cent of the original rate. Thus, indicating free radical mechanism as the main route of pyrolysis, with a limited amount of molecular rearrangement.

During the pyrolysis of hydrocarbons, particularly at high temperatures, acetylene is one of the products. It is generally accepted that the formation of acetylene is from a molecular rearrangement of ethylene. This is supported by the fact that NO_2 additions do not affect the decomposition rate of ethylene to acetylene. Propylene and heavier olefins may be a source of acetylene formation, however, it is felt that the mechanism of breakdown is first to ethylene, followed by the ethylene breaking down to acetylene.

Another product of hydrocarbon pyrolysis is methane, which, at high temperatures may be converted into acetylene. This conversion follows through the production of ethane as a stable primary product, followed by its decomposition through ethylene to acetylene. Several mechanisms have been proposed for the initial pyrolysis step. Some of these mechanisms involve the decomposition of methane to form methylene radicals and a molecule of hydrogen, followed by the reaction of a methane molecule and a methylene radical to form ethane. Methylene radicals have been detected in the reaction of methylene dibromide with sodium vapor. However, several studies of methane pyrolysis have failed to detect the formation of any methylene radicals (only the methyl radicals were found present).

Other radicals have been detected in mixtures of methane and hydrogen cracked in electric arcs. Low energy arcs produced methyl, methylene and methyne radicals, while high energy arcs produced only methyne and C_2 radicals. The presence of these radicals would suggest several possible mechanisms involving their interactions. However, since these methylene, methyne and C_2 radicals have not been detected in thermally cracked methane, the possible mechanisms will not be discussed here.

TABLE 1

PYROLYSIS MECHANISM

Primary Reactions

1. Molecular Rearrangement:

$$C_3H_8 \longrightarrow C_2H_4 + CH_4$$
$$C_3H_8 \longrightarrow C_2H_6 + H_2$$
$$2\ C_3H_8 \longrightarrow 2\ C_2H_6 + C_2H_4$$
$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

2. Free Radical Mechanism:

$$CH_3\ CH_2\ CH_3 \longrightarrow CH_3\ CH_2^* + CH_3^* \qquad \text{(Initiation)}$$

$$CH_3\ CH_2^* \longrightarrow CH_2{=}CH_2 + H^*$$
$$CH_3\ CH_2\ CH_3 + H^* \longrightarrow H_2 + CH_3\ CH_2\ CH_2^*$$
$$ \searrow H_2 + CH_3\ C^*H\ CH_3 \qquad \text{(Propagation)}$$
$$C_3H_8 + CH_3^* \longrightarrow CH_4 + (C_3H_7)^*$$
$$C_3H_8 + CH_3\ CH_2^* \longrightarrow C_2H_6 + (C_3H_7)^*$$

$$CH_3^* + H^* \longrightarrow CH_4$$
$$2\ CH_3\ CH_2^* \longrightarrow C_4H_{10} \qquad \text{(Termination)}$$
$$2\ CH_3^* \longrightarrow C_2H_6$$

Secondary Reactions

1. Molecular Rearrangement Forming Acetylene:

$$C_2H_4 \longrightarrow C_2H_2 + H_2$$

2. Free Radical Reactions With Methane:

$$CH_4 \longrightarrow CH_3^* + H^* \qquad \text{(Initiation)}$$

$$CH_3^* + CH_4 \longrightarrow C_2H_6 + H^* \qquad \text{(Propagation)}$$
$$CH_4 + H^* \longrightarrow CH_3^* + H_2$$

$$2\ CH_3^* \longrightarrow C_2H_6$$
$$CH_3^* + H^* \longrightarrow CH_4 \qquad \text{(Termination)}$$
$$2\ H^* \longrightarrow H_2$$

In mixtures with free radicals present, the initiation step is not necessary.

FLAME PROPAGATION IN GASEOUS MIXTURES

The initiation and propagation of a flame in a gaseous mixture containing a fuel and an oxidant is through the formation and reaction of atoms and free radicals in and near the flame front. Spectrographic studies of flames(17) have indicated the presence of C_2, CH, and OH radicals, and it may be assumed that O, H, CH_3, and many others exist. The presence of these radicals and atoms is explained by theories which fall into the two general classifications of thermal theories and diffusion theories.(18)

Thermal theories explain the presence of the atoms and free radicals as being the result of heat, transferred from the flame front, causing the dissociation of molecules. In opposition to this, the diffusion theories maintain that the particles are formed in the flame and diffuse into the colder layers of gas. Measurements of the OH concentration, by spectrographic methods, in acetylene-air and acetylene-oxygen flames have indicated concentrations far in excess of those calculated from thermal equilibrium considerations.

Hydrogen atoms would probably diffuse more rapidly than OH radicals and it is reasonable to assume that these would be the most effective chain carriers in the oxidation of hydrocarbons. Calculated results have indicated that the hydrogen atom concentrations in hydrogen-air and hydrocarbon-oxygen flames are in the order of 0.001 to 0.01 atmospheres partial pressure, assuming a diffusion mechanism controls. This is about ten times the partial pressures calculated by thermal considerations.

Several experiments have been designed in attempts to differentiate between thermal and diffusion mechanisms. One such study has involved the determination of burning velocities(19) of various fuels in the presence of helium and argon as diluents. Thermal theories predict that the ratio of burning velocities in the two mixtures is proportional to the square root of the ratio of the thermal conductivities. The diffusion theories predict dependence upon the square root of the diffusion coefficients of the important chain carrier. If two or more atoms or radicals are important, then the velocity ratio will be a function of some mean diffusion coefficient. As shown in Table 2, the ratio of burning velocities appears to depend upon the diffusion mechanism for all gases investigated except hydrogen, which does not follow either mechanism.

TABLE 2

Comparison of the ratios of the burning velocities (V_b) of mixtures containing helium to the burning velocity of mixtures containing argon, using the square root of the thermal conductivities (k) and the square root of the diffusion coefficients (D).

FUEL	% FUEL	% INERTS	V_b	$\sqrt{K}$	$\sqrt{D_H}$	$\sqrt{D_{OH}}$	$\sqrt{D_O}$
C_2H_2	8	78	1.61	2.69	1.30	1.39	1.41
	10	71	1.54	2.67	1.28	1.38	1.39
	13	69	1.55	2.64	1.27	1.35	1.37
CO*	50	20	1.09	1.37	1.06	1.07	1.08
	37	40	1.28	1.95	1.13	1.15	1.18
H_2	21	68	2.40	1.94	1.32	1.47	1.51
CH_4	10	71	1.39	2.65	1.29	1.39	1.41
C_2H_4	6	75	1.42	2.71	1.24	1.42	1.44
	7.7	73	1.43	2.70	1.23	1.40	1.43
	10	71	1.46	2.68	1.22	1.38	1.41

* Containing water vapor.

Combustion in systems not containing hydrogen show increases in burning velocities upon the addition of small amounts of water or hydrogen, whereas, systems containing hydrogen are not greatly affected. In some cases, however, the thermal theories may be applied with results equal to the diffusion theories, as has been found in the study of ethylene-air-nitrogen mixtures.

Investigation of the effect of diluent gases on the upper limit of inflammability of hydrogen-air-inerts and hydrogen-nitrous oxide-inerts have indicated a dependence on diffusion. The addition of argon, nitrogen or helium lowered the thermal conductivity of the resulting mixture in all cases. From this, thermal theories would indicate a lowering of the limit flame temperature. This was found to be true for the mixtures containing nitrogen or argon. However, with helium, the limit flame temperature increases. This may be explained by the fact that in the helium mixtures the diffusion coefficients, increased, whereas argon and nitrogen lowered the diffusion coefficients, thus indicating the possibility of a diffusion controlling mechanism.

Surface Combustion Burners

At relatively low temperatures, (below 1000 °F), most surfaces are not catalytic to combustion reactions. Some surfaces become catalytic at higher temperatures, stabilizing combustion on or very near the surface so as to produce no, or very little, visible flame. Ceramic surfaces coated with certain mixtures of metals (eg. platinum-aluminum combinations) can be used to stabilize combustion at temperatures of 1400 to 1600 °F. From 1600 to 1800 °F and higher most uncoated ceramic surfaces exhibit a stabilizing effect on combustion.

This stabilizing effect of ceramic surfaces is used in the design of surface combustion burners. With these burners, a hot incandescent surface is produced. Heat is transferred mainly by radiation, rather than by convection as is the case with most common types of burners.

The action of the surface on the combustion may be explained in light of both the thermal and diffusion theories of combustion and, in some cases, partly by the effect of turbulence on flame velocities. With a surface combustion burner, burning a premixed stoichiometric mixture of fuel and air (or oxygen), the stabilizing effect of the ceramic surface and the increasing effect with increasing surface temperature can be observed. At low temperatures, when

the burner is first lit, the flame is usually similar to the flame produced by a Bunsen burner; blue in color with the main part of the combustion occurring at some distance from the surface. As the surface heats up to full operating temperature, the flame gradually recedes onto the surface and becomes lighter in color and less visible. (The apparent disappearance of the blue flame is probably due to the intense luminescence of the ceramic surface.)

The changing combustion characteristics are not only noticeable by visual means but are also evident in the sound emitted by the burners. Upon lighting, the burners create very little sound, with only the occasional popping sound produced as the flame fluctuates across the burner face. As the burner heats up, the popping sound gives way to a low roaring sound which gradually increases in intensity with increasing surface temperature. At full operating temperature some surface combustion burners emit a sound similar to that of a distant jet engine.

The improvement in combustion with increasing temperature may also be observed by following the oxygen content of the combustion products. As the surface temperature rises the amount of oxygen present decreased, with a minimum reached when the burner is at full operating temperature.

Most surface combustion burners are similar in construction, consisting of a metal shell faced with a refractory burner block. The premixed gases are introduced into the shell, forced through the burner block, and burned on the external surface. Burners of this type may be divided into three general groups, depending upon the design of the burner block:

i. porous refractory diaphragms;
ii. impermeable refractory burner blocks containing tunnels or ports of constant or varying diameter;
iii. burner blocks having ports situated in such a manner as to direct the gas stream onto a refractory surface.

The burners constructed with a porous refractory diaphragm utilize a burner block made from a material having a high porosity and low thermal expansion. In these burners, combustion occurs within the small interstices on the external surface of the porous material, to produce little or no flame.

These burners would tend to favor a thermal theory of combustion since the higher thermal conductivity of the refractory would increase the rate of heat transfer to the incoming fuel mixture, thereby increasing the rate of temperature

rise within the gas and giving a flatter reaction zone. It is possible that some of the free radicals and atoms formed in the combustion zone would diffuse into the unburned gases. However, the tortuous path of the gas and the relatively small diameter of the pores would most likely limit the amount of diffusion possible. The flow of the gas through these pores may also result in considerable turbulence which would tend to increase the flame velocity and help stabilize the flame on the burner surface.

Operating conditions for these burners depend upon the conduction of heat through the refractory to the incoming gases. At very high gas rates, the rate of heat transfer would not be high enough to give sufficient temperature rise to initiate and maintain combustion on the burner surface. In such a case, most of the combustion would occur at some distance from the surface and would be similar to that attained with a Bunsen burner. Increasing the gas flow beyond this rate would blow the flame off the surface completely and eventually the flame would be extinguished. A lower limit exists when the gas flow is too low to transfer heat away at a high enough rate. In this instance the initiation of the combustion would occur too soon and allow the flame to recede into the burner block. When the flame recedes, the temperature on the back of the block usually continues to rise until combustion occurs within the burner shell. This is known as flash back. These operating limits would depend upon the fuel mixture used and upon the type of ceramic used for the burner block.

The second class of burners uses a nonpermeable refractory burner block through which numerous ports have been drilled. The shape and size of these ports may vary considerably, ranging from small and of uniform diameter, to relatively large, with varying diameter. Burners of this type having numerous small diameter openings would tend to be similar in behavior to the porous refractory diaphragm burners.

The burner used in the work described in this thesis was a tunnel type burner, with diverging ports.

Both thermal and diffusion mechanisms may hold for combustion within the tunnels. The hot incandescent surface transfers heat to the relatively cool unburned gas and also serves as a source of free radicals and atoms which can diffuse into the unburned gases. Some turbulence may also occur within the tunnels and help stabilize the flame on the tunnel walls.

The construction of these burners is, in some respects, similar to the porous burners. The portion of the burner block enclosed within the shell usually

contains numerous small openings leading to the tunnels. The gas issues from these openings at relatively high velocities. This feature limits the amount of heat that may be transferred to the gas as it passes through the first part of the block and at the same time lessens the danger of flash-back occurring. The effect of the high velocity may also produce turbulence which would increase the rate of heat transfer from the hot walls to the cooler unburned gases. This turbulence would also assist the diffusion of the highly active particles into the gas.

The burners using impingement as a means of stabilization, are usually constructed with the burner block contained within the shell, and having numerous small diameter openings. These openings are positioned in such a manner that the jets of gas issuing from them will impinge upon refractory surfaces. This impingement produces turbulence within the gas. The stabilization of flames by turbulence is most likely caused by both the higher rates of heat transfer and the increased diffusion of active particles.

EXPERIMENTAL EQUIPMENT

Furnace

The furnace, shown in cutaway sketch, Fig. 4, was constructed within a 36-inch cubical steel shell. This size was based on burner dimensions and the calculated thickness of commercial refractory brick required to give an external shell temperature of 100 °F when the burners were operated at 3000 °F. One-half inch steel plate was used for the shell and all bolted flanges were made from 2.5 inch angle iron. The top, bottom and front of the furnace were separate plates; while the back and two sides were welded into a solid unit. This shell served to support the furnace, seal the combustion-reaction zone from the atmosphere, and protect the surroundings from possible explosions.

The burners, manufactured by Radiant Heating Limited of London, England, were a tunnel type radiant heating burner designed to release 2000 to 3000 BTU per hour per square inch of tunnel opening, at operating temperatures of 2300 to 2600 °F. The overall burner block was 6.4 inches wide, 12.25 inches long, and 4.31 inches thick, and projected approximately 2 inches from a cast iron housing. Three refractory bricks, each containing 15 tapered diverging tunnels, were cemented together to form the burner block. Each tunnel was fed by a ceramic fuel inlet tube 1-13/16 inches long and with an inside diameter of 1/8 inch. The tunnels diverged from 5/8 inch diameter at the inlet, to 51/64 inch diameter at the outlet.

A cast iron housing enclosed the back of the burner block and left a space 1-5/8 inch wide behind the distributor block. A 1-1/4 inch pipe thread, for a fuel pipe, was tapped in the center of the back of the housing. Inside the housing, 3/16 of an inch from the fuel inlet and centered with the fuel inlet, was a baffle plate 2 inches wide and 3 inches long. The purpose of this plate was to act as a velocity breaker for the incoming fuel and to give an even distribution of the fuel to the tunnels.

A 1/8 inch pipe tap was also located in the back of the burner housing. This tap was used to install a thermocouple, with the tip touching the back of the distributor block.

Each burner was mounted on specially fabricated steel stands. In a mounted position, the burners were 4.5 inches (the width of one refractory brick) above the furnace floor and vertical, with the 6.4 inch width horizontal. Mounting of the burners in this manner dictated the location of the fuel inlets, thermocouples, and the pyrometer and lighting ports.

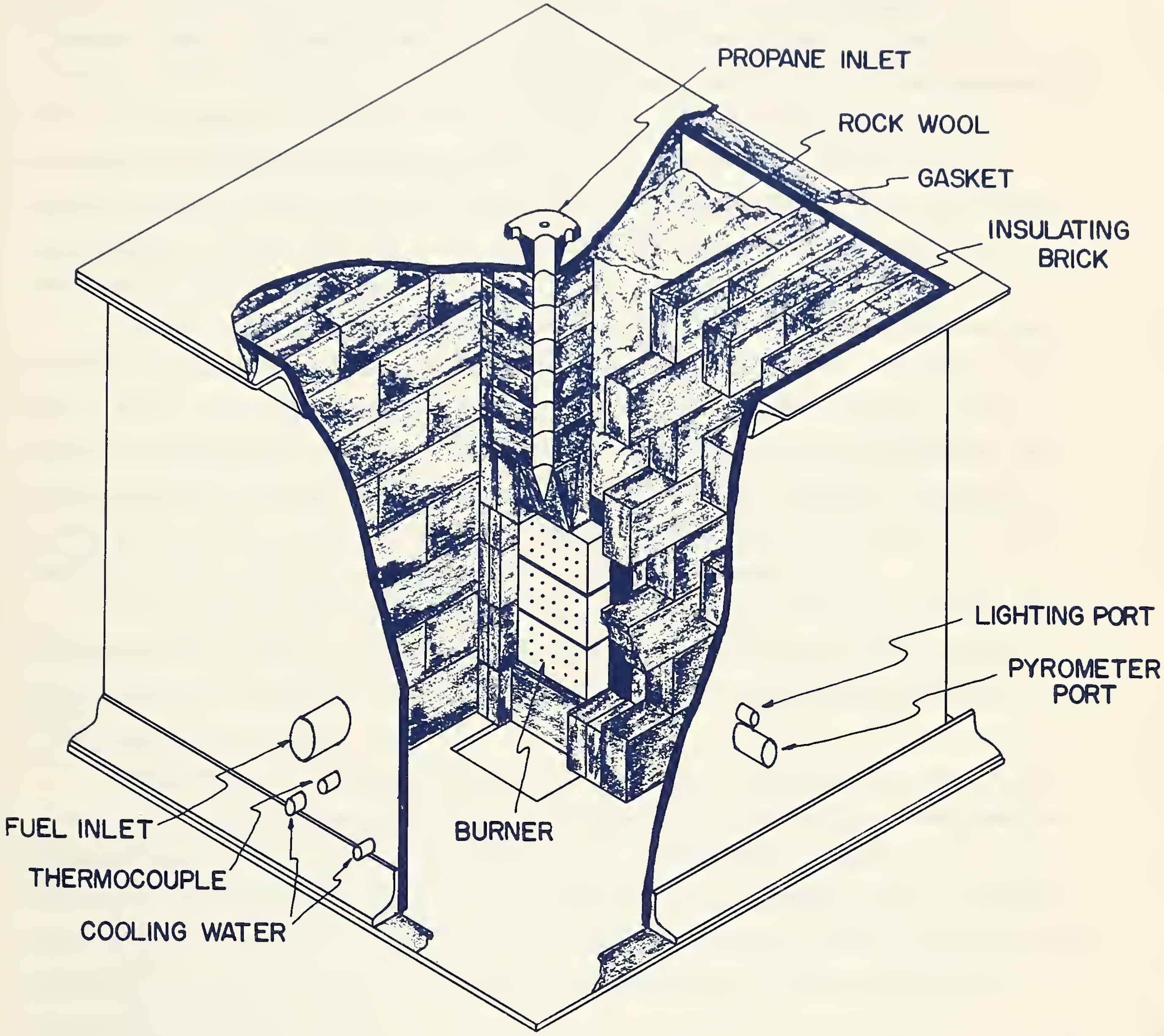


Figure 4. Cutaway View of the Furnace

Original plans were to cool the burner shells by using copper cooling coils cemented to the backs of the shells with a cement having a high heat transfer coefficient.

The front and back plates were fitted with identical connections for fuel, cooling water, nitrogen purge and thermocouple connections. A 2.5-inch half coupling, centered and located to be 10-5/8 inches above the furnace floor, was welded on the outside of the two plates. Through the center of the couplings a hole was drilled large enough to give approximately 1/8 inch clearance around a 1-1/4 inch pipe. A teflon ring, cut to fit inside the couplings and snugly around a 1-1/4 inch pipe, was used as a sealing ring. This ring was compressed, to form the seal, by a 2-1/2 inch hexagonal bushing which had been reamed out to give 1/8 inch clearance around a 1-1/4 inch pipe.

Two 3/4 inch half couplings, welded below and on each side of the fuel inlet, were used as cooling water and nitrogen purge inlets. A tee, fitted into one of the couplings, was used to allow entry of the nitrogen and a 1/4 inch copper tube to the cooling coils on the backs of the burners. The other coupling was used simply as an inlet for copper tubing to the coil. Compression type copper fittings, which had been reamed out to pass 1/4 inch copper tubing, were used to seal the tubing in the couplings.

The cooling coils were removed from the burners after some preliminary tests had been made, and at the same time, it was felt that the nitrogen purge was not necessary. At this time, the coils were removed and the couplings were plugged.

One side of the furnace was fitted with three thermocouple connections (each 3/4 inch couplings). These fittings were placed to allow temperature measurement at the top, middle, and bottom of the reaction zone. The other side was fitted with a quartz glass pyrometer port, equipped with a nitrogen purge, at the center of the plate and about 10 inches above the furnace floor. Immediately below the pyrometer port, a lighting port with a removable plug was installed.

The bottom plate had an 8-inch square opening, at its center, for a gas outlet. A 10-inch square flange (made from 2-inch angle iron) was welded on the outside of the plate and centered around the opening. A quench tube was designed to fit onto this flange.

A 2-inch diameter hole was located in the center of the top plate. On the outside, and around this hole, a 2-inch welding neck flange was fitted. A 2-inch diameter stainless steel feed tube was fabricated to slide into this flange and extend approximately 10 inches into the furnace (ending about 8 inches from the top of the burners). Copper cooling coils were cemented to the outside of the top as a precautionary measure against excessive heating of the plate. These coils were later abandoned when it was found that they were not necessary.

In assembling the furnace, the bottom plate was positioned on the second floor of the Special Equipment Well. The section of the floor, where the furnace was mounted, was specially reinforced to carry the weight of the furnace. Once the plate was in position, it was spot welded to the supporting beams. The unit, consisting of the back and two sides, was then bolted into position. Asbestos gasket material and a high temperature sealing compound were used to seal the flanges.

A 12.25 inch wall of refractory brick was laid on each side of the furnace, leaving a corridor slightly wider than the burner shell, through the center. From the outside to the center, each wall consisted of: two rows of G-20 brick; two rows of G-26 brick; and one row of G-26 brick with G-28 brick used in the center where the highest temperatures would be attained. (The brick designation refers to the maximum operating temperature in hundreds of degrees Fahrenheit; i.e. G-26 refers to a brick designed for use at a maximum temperature of 2600 °F.) Holes, to accomodate the pyrometer and lighting ports, and the thermocouples, were drilled through the bricks.

The burners were installed in each end of the corridor, facing the center, and were free to move back and forth. When the burners were in position, specially cut pieces of G-32 brick were fitted around the burners to insulate the burner shell and to close in the reaction zone to the width of the burners and to the top of the burners (6.4 inches by 12.75 inches high by the spacing of the burners). Over top of the burners, a layer of interlocking pieces of G-32 brick was placed. Layers of G-28 and G-26 brick were used to build up the center to the top of the furnace. A hole for the feed inlet was drilled through these layers.

With the interior of the furnace assembled, the front plate was bolted into position, the fuel and cooling water lines, thermocouples and the nitrogen purges were connected up. The top was then bolted on and the stainless steel feed tube inserted.

When the cooling coils on the burners and the nitrogen purge were remove, the space behind the burners was filled with loose rock wool insulation.

All seals, gaskets and couplings were checked for leaks by testing with a soap solution when the furnace was under pressure. Any leaks found were sealed with an epoxy resin. With the furnace under vacuum while the resin was applied, the resin was drawn into pinholes and fine cracks to make an excellent gas tight seal.

Air Supply

The air source for the burners was the normal service air supplied by the power plant. Available at about 80 psig., it was originally hoped that the supply would be large enough to feed the burners and an ejector on the exhaust stack. Later use of the air showed that the supply was not as great as originally anticipated and, because of this, only the burners were operated on the existing supply.

Since the air contained an unusual amount of entrained water and oil-water emulsion, it was necessary to install a small, tangentially fed, knock-out vessel and a porous stone filter. Both of these units were drained to a collecting vessel maintained at air-line pressure. With periodic draining of the collected water, the air was maintained at a reasonably dry level. However, during periods of high humidity some carry-over was encountered.

Reduction of the air pressure was attained by using two volume boosters, controlled at a set pressure with an air set valve. From the air boosters, the air flowed through control valves to two orifice meters. The meter runs were constructed from 2 inch Schedule 40 pipe fitted with orifice flanges in accordance with the American Gas Association specifications, as set in the A.G.A. Report No.3. Water manometers were used to measure the differential pressures across the orifices, and a mercury manometer was employed, with a manifold, to measure the upstream static pressures. Temperature of the air was measured by thermocouples installed in the downstream meter runs.

The air was then piped to venturi type mixers where it mixed with natural gas to produce the premixed fuel for the burners.

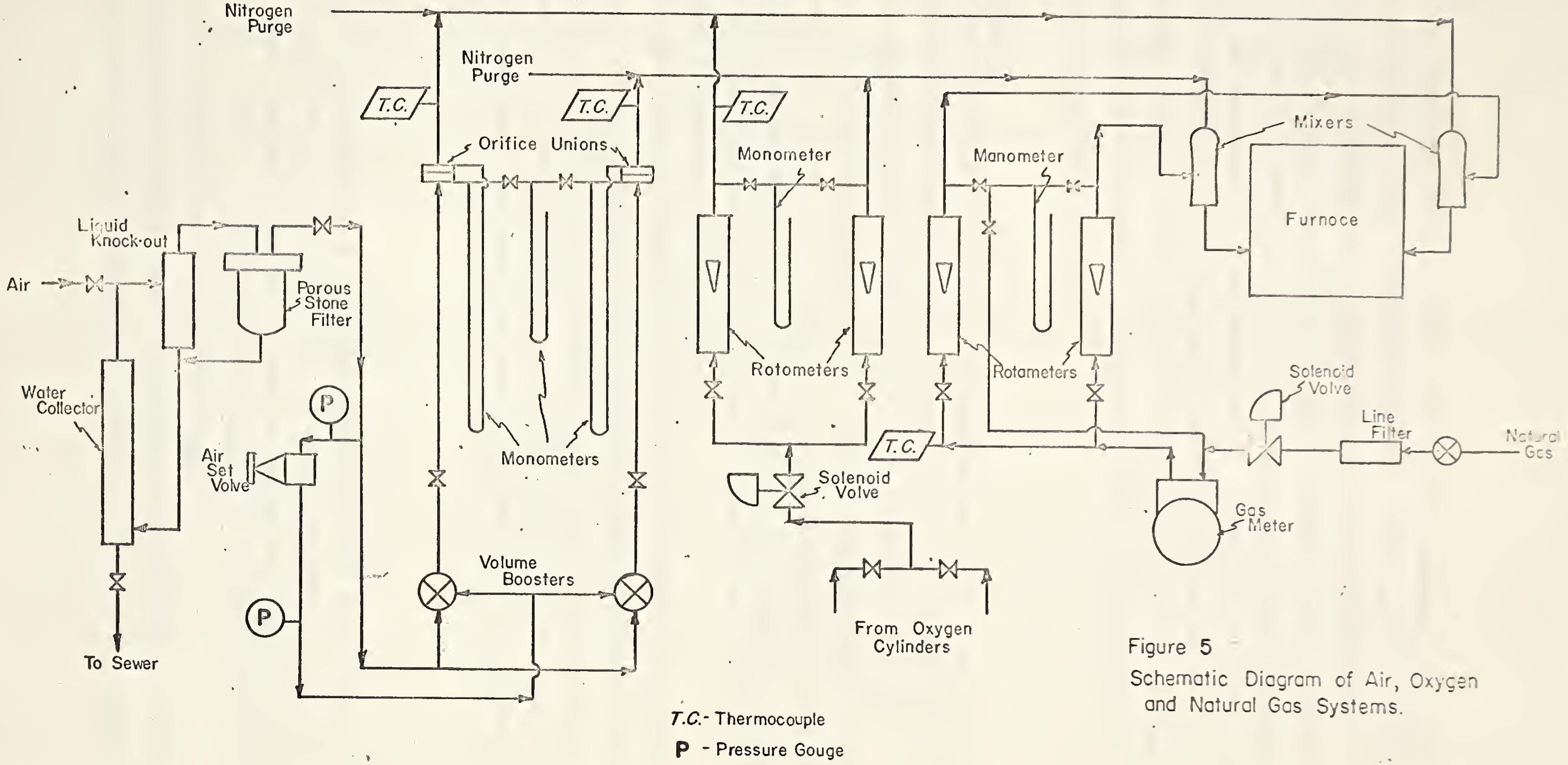


Figure 5
Schematic Diagram of Air, Oxygen and Natural Gas Systems.

Oxygen Supply

Oxygen was supplied from cylinders, fitted with pressure regulators, connected to a manifold. From the manifold, the oxygen passed through a solenoid valve to two rotameters. These rotameters were Fisher-Porter instruments with a maximum capacity of 11 SCFM (standard cubic feet per minute) of air, at 70 $^{\circ}$F and 14.7 psia. Flowing pressures were measured by a mercury manometer connected to the rotameters by a manifold, and the flowing temperature was measured by a thermocouple installed in one of the flow lines. From the rotameters, the oxygen was fed into the air lines immediately upstream from the venturi mixers. At this same point, lines from the nitrogen purge system were tied in.

Natural Gas Supply

The natural gas used for fuel in the burners was taken from the mains, supplied by Northwestern Utilities, at about 6 psig. From the main line, the naural gas passed through a line filter and a solenoid valve into a bellows-type, positive displacement meter. The gas was then piped to two rotameters, and from there, to the mixers. Flowing temperature was measured by a thermocouple installed in the line leading to the rotameters. A mercury manometer, connected by a manifold to the two rotameters and the bellows meter, was used to measure flowing pressures.

In the lines from the rotameters to the mixers, pressure regulators were installed. These regulators were originally intended for use with a proportional mixer. However with the mixers used, it was found the the regulators would not operate properly. In order to maintain an open position during normal operation, the regulators were supplied with line pressure to the diaphragms.

Propane System

The propane was stored in a 1000 U.S. gallon storage tank located outside of the Engineering Building. This tank was equipped with filling connections, vapor removal fittings, a pressure gauge and a volume indicator on the top of the tank. A liquid removal connection, fitted with an excess flow valve, was located on the bottom of the tank.

Liquid propane was carried from the tank into the building by a Type K copper line, one-half inch in diameter, enclosed in a one inch steel line.

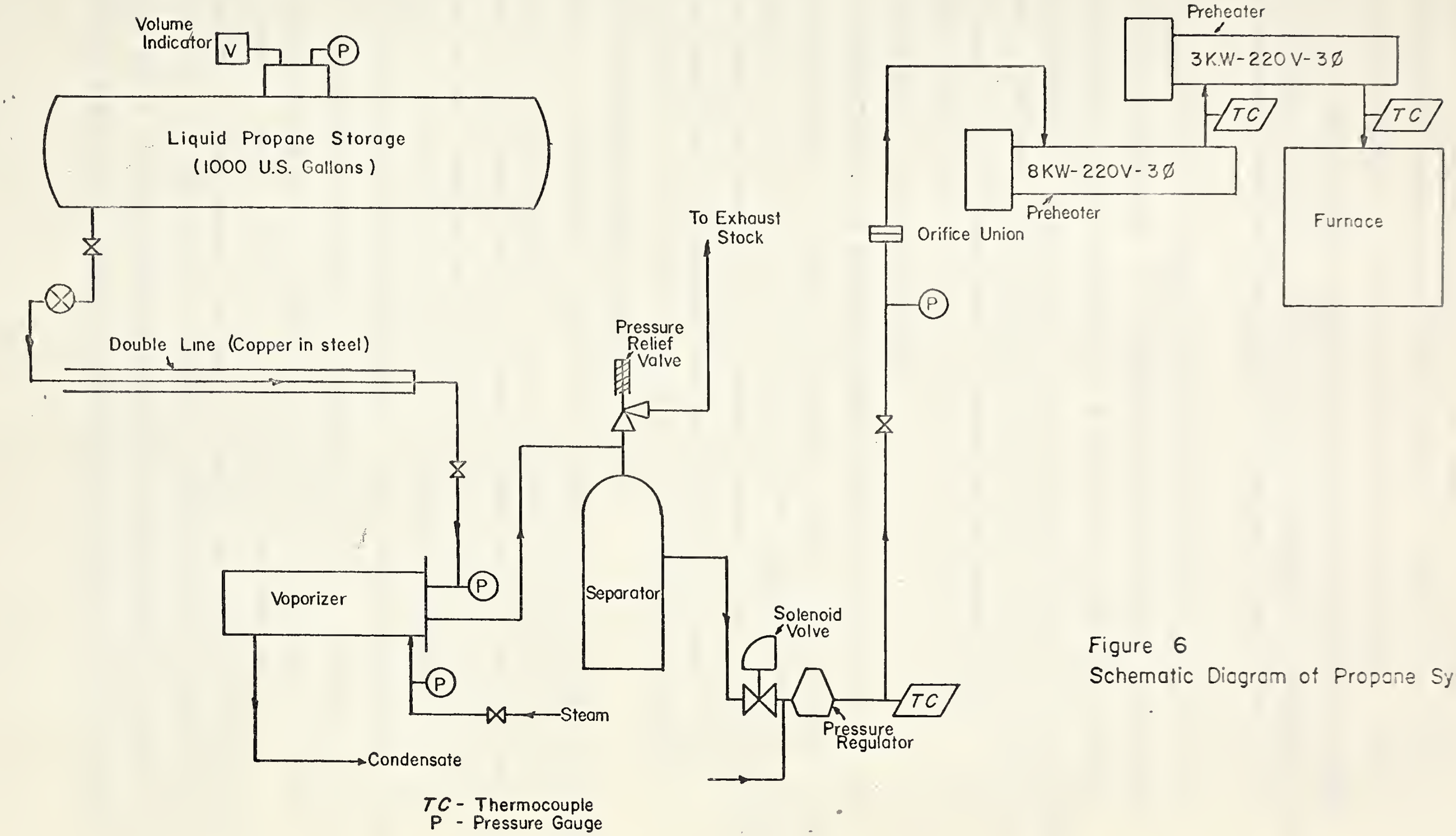


Figure 6
Schematic Diagram of Propane System

The steel line was sealed to the copper line inside the building, while the outside end remained open to atmospheric pressure. Adapters for copper-to-standard pipe were welded to the copper line with silver solder. From the copper line to the panel-board, one-half inch Schedule 80 pipe, with 2000 pound W.O.G. fittings was used. This line was installed in accordance with instructions received from the Department of Industries and Labour, Gas Branch.

At the panel-board, the liquid propane was throttled through a valve into a steam heated vaporizer. The vaporizer was constructed from copper tube, with twelve tube passes enclosed in a steel shell, and had a large heat transfer capacity in comparison to the vaporization load. Low pressure steam was fed to the shell surrounding the copper tube. From the vaporizer, the propane passed into a surge-tank to remove any entrained liquid. This surge-tank was fitted with a spring loaded relief valve. The outlet of the valve was connected to the exhaust stack.

From the surge-tank, the propane passed through a solenoid valve and a pressure regulator to a critical flow orifice. The pressure at the orifice was maintained at a chosen value by a control valve upstream from the orifice. The static pressure was measured by a common pressure gauge. A thermocouple was installed immediately downstream from the regulator to measure the flowing temperature. At the downstream side of the pressure regulator, a line from the nitrogen purge system was tied in.

Originally, it was hoped to measure the propane flow by using a rotameter. During the testing of the furnace it was found that decompositon of the propane entering the furnace set up a pressure wave which travelled back down the pipe to the rotameter and blocked the flow. When this pressure wave dissipated, the rotameter float rose to the top of the scale and was immediately depressed by a new pressure wave. This rapid oscillation of the float made it absolutely impossible to read the flow rate. Because of the sonic velocity obtained in the orifice of a critical flow meter, this type of measuring device was installed, and proved to be satisfactory.

After metering, the propane was passed through two stages of preheating and into the furnace. The propane preheaters were specially ordered electrical heaters, wired in a parallel-delta pattern and designed to operate on 230 volts, three phase A.C. Initial preheating was done in an 8 KW heater,

while the second stage heater was 3 KW. Temperatures were measured by thermocouples at the outlet of each heater.

Water Quench

Immediately below the furnace, the gases passed into a stainless steel tube, six inches in diameter. This tube was equipped with spray nozzles from which water was sprayed directly into the hot gas stream. At the top of the quench section, four flooding nozzles were placed to direct a steady stream of water onto the walls of the quench tube. Six spray nozzles were located immediately below the flooding nozzles. When these nozzles were found to be inadequate to cool the gas down to a reasonable temperature, four more nozzles were placed at various points down the quench tube. With the increase in spray capacity the gases were quenched to about 185 °F.

For the last run with the furnace, the spray nozzles and the flooding nozzles were removed to give a longer soaking period for the cracked gases. To cut down the heat losses through the tube, the interior was lined with insulating brick to about one foot below the furnace. During the run the outside of the tube became exceedingly hot and it was necessary to mount spray nozzles around the outside.

The temperature at the bottom of the quench tube was measured by a thermocouple. A pressure tap was also installed and connected to the static pressure manometer of the off-gas orifice.

Cooling Tower

The gas leaving the quench passed into the bottom of a small tower packed with ceramic raschig rings. In this tower the gas flowed upward countercurrent to a flow of water. This tower was found to be too small for the quantity of the gas handled, being easily flooded, and caused serious pressure fluctuations within the furnace. Because of this, the packing was removed from the tower and no further cooling of the gases was done. A larger cooling tower was installed for the last three runs made.

A considerable amount of carbon was carried in the off-gas from the furnace. This carbon was not water wettable and could not be washed out of the gas. To combat this problem, several surfactants were tested for their ability to wet down carbon particles. Most of the surfactants tested

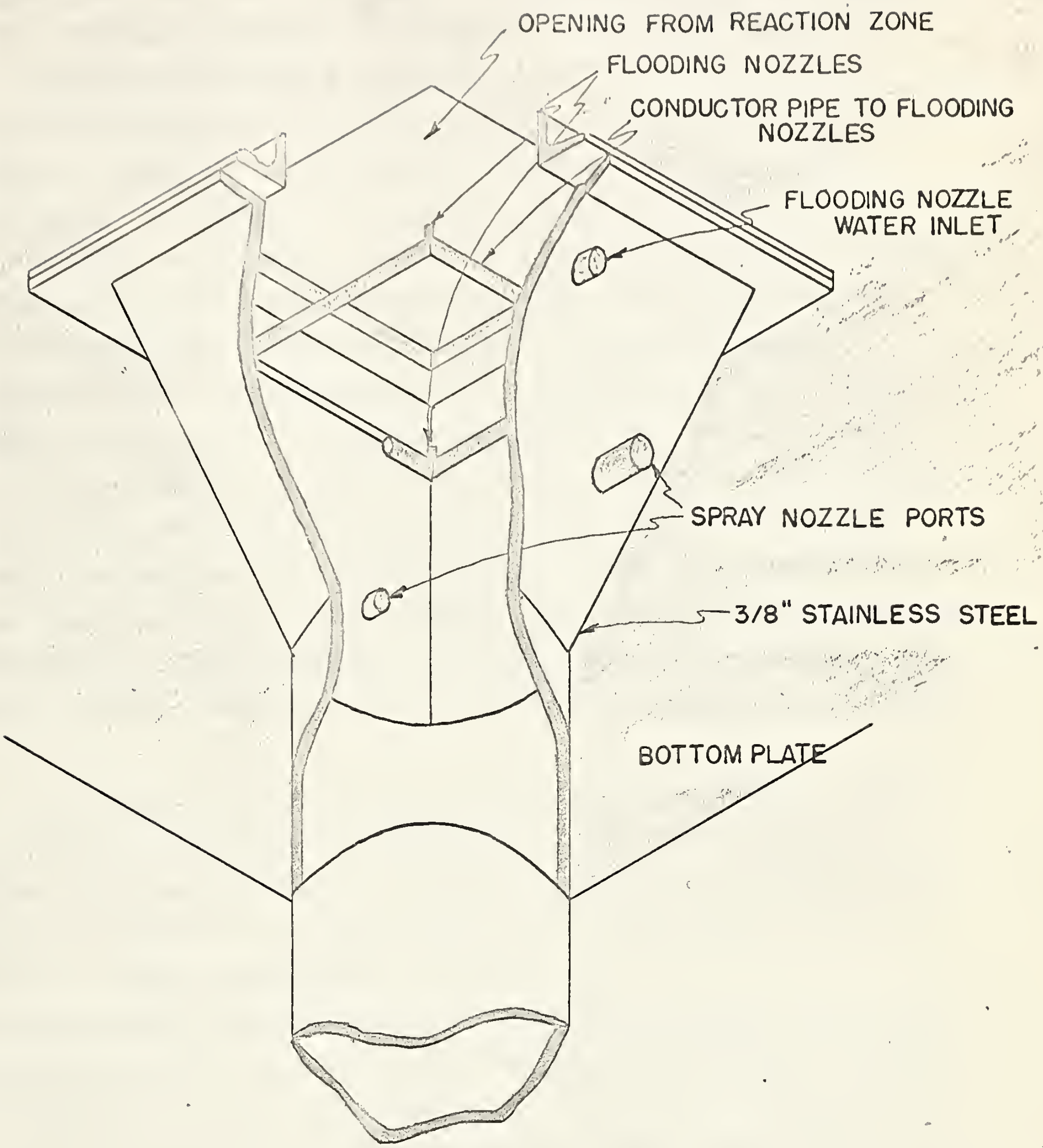

OPENING FROM REACTION ZONE
FLOODING NOZZLES
CONDUCTOR PIPE TO FLOODING NOZZLES
FLOODING NOZZLE WATER INLET
SPRAY NOZZLE PORTS
3/8" STAINLESS STEEL
BOTTOM PLATE

FIGURE 7.

TOP OF QUENCH CHUTE
1/5 SCALE

would wet the carbon to some extent, however, they were slow acting and were required in fairly high concentrations. The surfactant chosen was one marketed in Canada by Dowell of Canada, under the code name of F-33. This surfactant was found to be suitable in concentrations of about one part per five thousand parts water, however to insure rapid wetting of the carbon, higher concentrations were used.

For the most efficient use of the surfactant, it was felt that a spray of water, containing the surfactant, opposing the off-gas flow would be suitable. To eliminate the need of mixing large quantities of surfactant solution, an injection system was designed to mix water flowing to the spray nozzles with a concentrated solution. The concentrate was stored in a discarded gas sample bomb of about 7.5 gallons capacity. A constant injection rate was maintained by air pressure supplied from an air set valve to the top of the storage container. The actual injection of the solution was through a small orifice into the main stream of water, with turbulence in the line relied upon to mix the solution thoroughly.

The spray nozzles for the surfactant were located in the bottom of the cooling tower, and were directed against the stream of off-gas entering. In the place of the ceramic packing, rock wool, supported on screens, was substituted in hopes of removing some of the carbon missed by the surfactant.

When the original cooling tower was found to be too small, a larger tower was ordered. This tower contained seven cubic feet of packing and had a baffle arrangement in the top section to remove any entrained water. Three runs were made with this larger tower and it was found to fill the requirements in cooling the off-gas to about 70 °F.

When the new tower was installed, the original tower was filled with crushed brick and the gas from the quench was piped into the top. The gas leaving the original tower at the bottom, was fed into the bottom of the larger tower. In the top of the original tower, three spray nozzles were installed and fed with the surfactant solution. This arrangement gave better contact between the surfactant solution and the gas, making it possible to remove more carbon.

The effluent streams leaving the quench and the two towers were piped to the basement of the equipment well where they entered a small open vessel which acted as a water seal. From the open vessel, the effluent drained to sewer.

Off-Gas Metering

From the top of the cooling tower, the gases entered a three inch pipe leading to the exhaust stack. In this off-gas line an orifice union was installed in accordance with the American Gas Association specifications. The pressure drop across the orifice was measured by a water manometer, while the upstream static pressure was measured by a mercury manometer. This static manometer was also used, with manifold connections, to measure the pressure in the bottom of the quench tube.

Exhaust Stack

The off-gases were ejected into the atmosphere through the exhaust stack leading to the roof of the Engineering Building. On equipment used previously, exit gases were forced into the stack by air or steam ejectors located inside the building. For this equipment it was felt that an ejector located on the exit of the stack would be more suitable.

The first ejector installed was designed to operate on high pressure air. Simultaneous operation of the ejector and the burners reduced the air supply from 80 psig. to about 30 psig. To overcome this difficulty, the ejector nozzle was redesigned to handle steam at 185 psig. Steam operated, the ejector was able to pull and maintain a vacuum of about 6 inches of mercury. Since this suction was more than required, a valve was installed immediately before the off-gas entered the exhaust stack to control the furnace pressure.

Nitrogen Purge System

In order to safeguard against possible burner damage and flash-back caused by high temperatures in the burner shells, a nitrogen purge system was installed. If the temperature in the burner shells reached a value higher than the limit thought safe, the system was designed to shut off the natural gas, oxygen and propane and turn on a flow of nitrogen to the mixers and the propane system.

This safety system was built around two Pyrotacs and solenoid valves. Each Pyrotac was connected to a thermocouple leading from the back of one of the burners. The internal circuit was designed to break an external circuit if the temperature reached a higher value than a predetermined limit set on the Pyrotac.

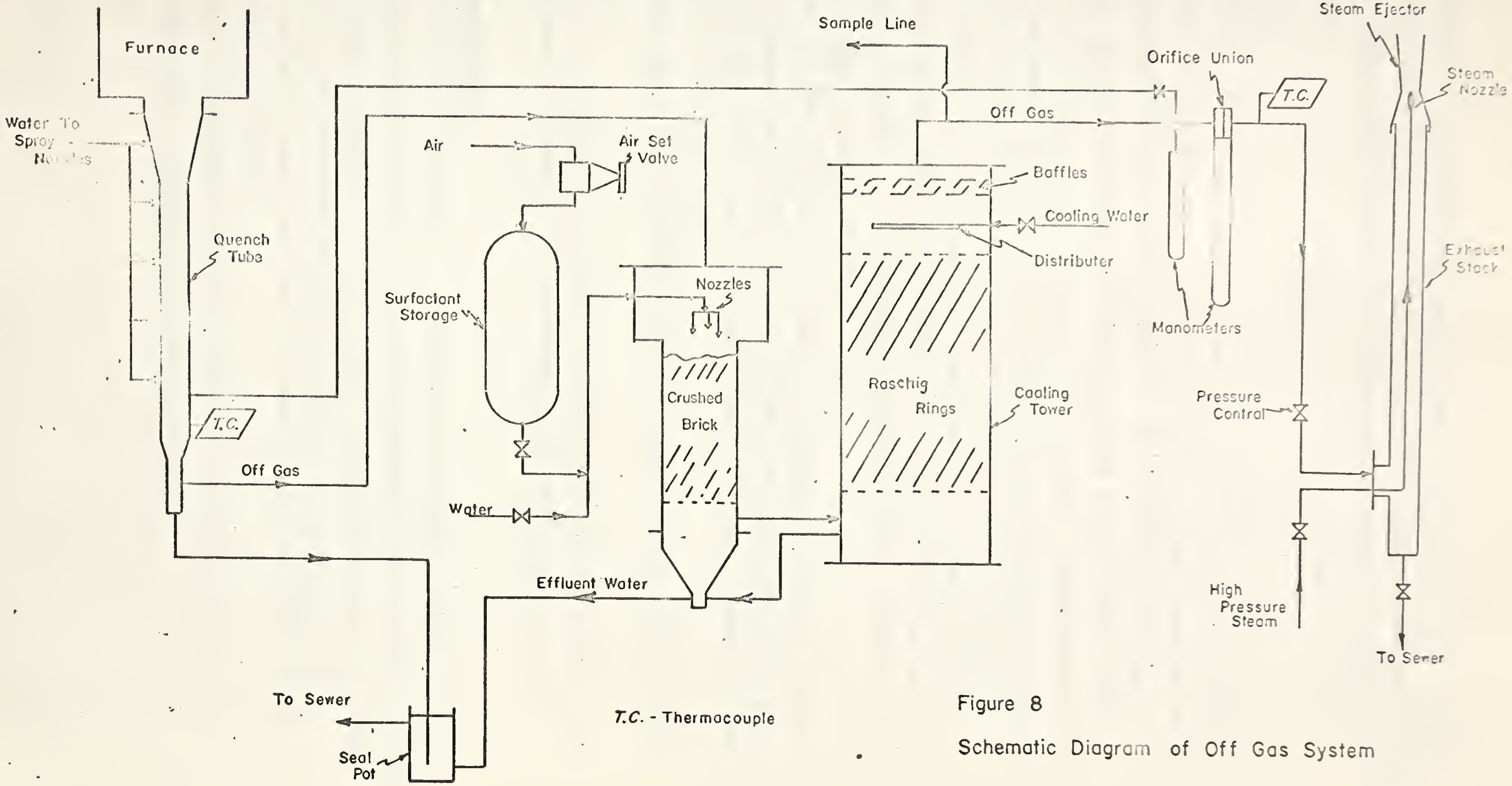


Figure 8

Schematic Diagram of Off Gas System

The electrical circuit was designed in such a way that if one or both of the Pyrotacs broke the circuit, the solenoid valves on the oxygen, natural gas and the propane closed, while the nitrogen was released by opening a solenoid valve.

Sampling System

A small side stream was removed from the off-gas by means of a small gas pump. From the off-gas line, the sample entered a small cooling section to condense some of the water vapor present. The condenser consisted of a coil of copper tubing, through which the gas passed into a small vessel. Surrounding the coil and vessel was an ice water bath. From the top of the vessel, the gas passed through a fiber glass filter to remove any entrained carbon. Water condensed out of the gas was collected in the vessel and drained to a seal pot. Remaining water was removed by a small column of Drierite before the gas entered the pump. From the pump, the gas split into three streams: one leading to a continuous recording gas gravitometer; and two streams leading to sample bottles.

One of the streams leading to a sample bottle passed through a column of Ascarite to remove carbon dioxide. From the Ascarite column, the gas passed into a sample bottle and out to an oxygen analyser. (Ascarite was used in only the last two runs.)

The second sample stream passed through a sample bottle into an Orsat Analysis unit.

A line from the natural gas system was also installed in order to run samples of natural gas through the gravitometer or the oxygen analyser.

Temperature Measurement

Temperatures were measured, at various points throughout the equipment, by Chromel-Alumel thermocouples. All of the thermocouples used were inclosed in stainless steel wells, and were fabricated at the University. The wells were tipped (with the thermocouple wires welded into the the tip) with either silver solder or stainless steel, depending upon the point of use and the temperatures expected.

All of the thermocouples used were tied into an eighteen point temperature indicator. A common cold junction was used.

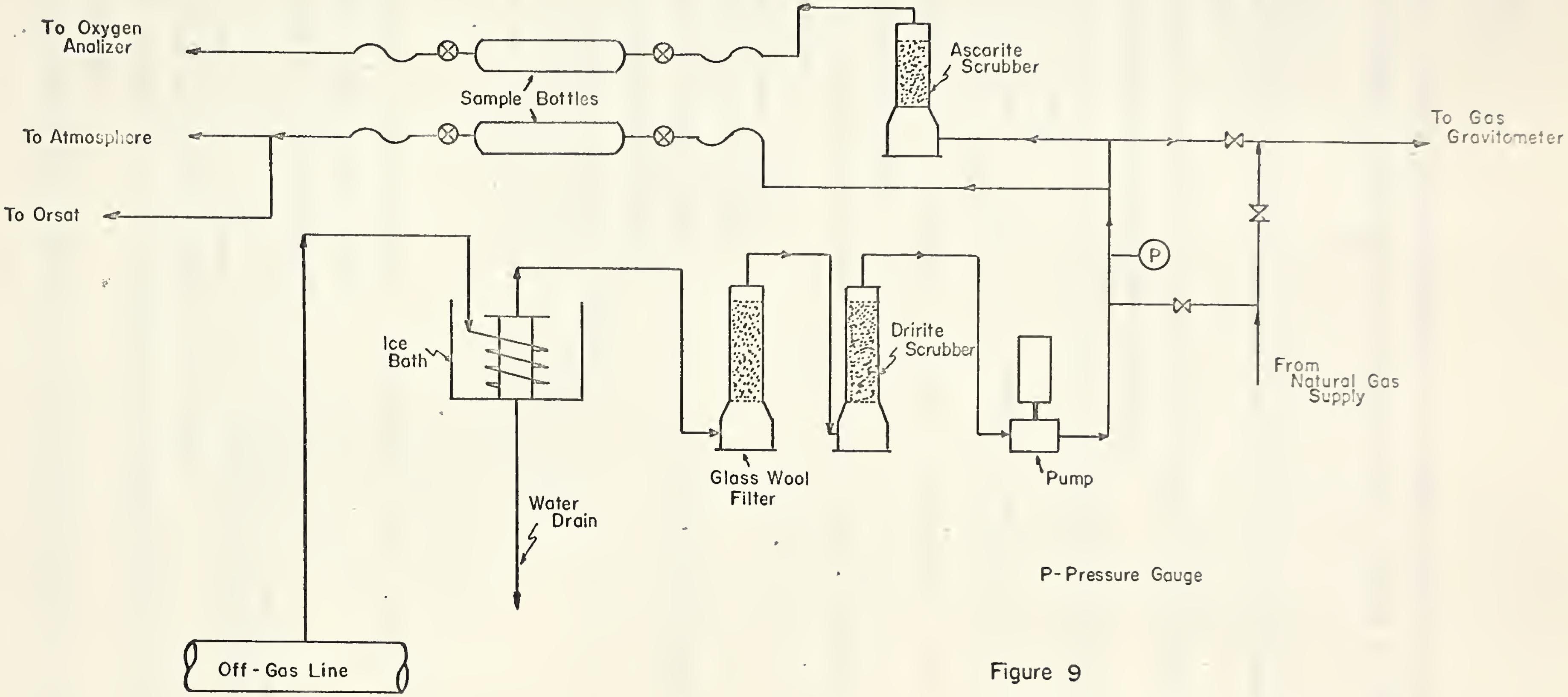


Figure 9
Schematic Diagram of Sampling System

OPERATING PROCEDURE

The equipment operating and maintenance procedure, which was found to be necessary and adequate during the experimental runs, was as follows.

Preliminary Work

1. Replaced glass wool, Drierite and Ascarite in off-gas sampling equipment.
2. Filled water condenser, on sample line, with ice and water.
3. Zeroed and recalibrated oxygen analyser.
4. Checked water receiver on air line: if necessary, water was blown down to sewer.
5. Installed oxygen cylinder, with regulator valves set to give 80 psig. output pressure.
6. Checked pressure on nitrogen cylinder: if necessary, a new cylinder was installed.
7. Turned on potentiometer and filled cold junction bath with ice and water.
8. Checked furnace lighter.
9. Turned on pyrotac system.
10. Switched on natural gas solenoid valve and started natural gas flow to the gas gravitometer.
11. Set up acetylene analysis equipment.
12. Checked and filled surfactant storage tank.
13. Checked and cleaned off-gas orifice run.

Start Up

1. Valves on all lines leading to the exhaust stack, except the water drain line, were closed.
2. High pressure steam was turned on to the ejector.
3. The valve on the off-gas line to the stack was cracked open.
4. Drain lines of the off-gas orifice meter were checked for carbon plugging and were sealed with water.
5. Air was turned on to the burners at a rate of about 15 SCFM to each burner.
6. Furnace pressure was adjusted to 0.2 inches of mercury vacuum.

7. Water to the cooling tower was turned on at a rate of about 4 gallons per minute.
8. Water, at the maximum available pressure, was turned on to the spray nozzles in the quench.
9. Sight port for the pyrometer was cleared with nitrogen.
10. Furnace lighter was installed and switched on.
11. Natural gas was turned on to one burner at a rate of 1.3 SCFM. When the furnace was lit (indicated by a rise in the quench chute temperature), the second burner was turned on.
12. The lighter was removed from the furnace.
13. Flow rates of air, natural gas, and oxygen (if required), were adjusted to desired rates. Furnace pressure was maintained at about atmospheric pressure.
14. Propane preheaters were turned on.
15. The oxygen analyser was switched to off-gas.
16. The furnace was allowed to heat up.

Once the furnace had warmed up to temperatures of the order of 2300 $^{\circ}$F, the propane feed was turned on. The following indicates the procedure used in starting propane feed to the furnace.

17. Low pressure steam to the propane vaporizer was turned on.
18. The pressure relief valve on the vaporizer was adjusted to about 100 psi.
19. Surfactant spray was turned on.
20. Liquid propane was allowed to flow into the vaporizer.
21. The flow of propane vapor to the furnace was set at the desired rate.
22. Pressure in the vaporizer was balanced at about 80 psig. by controlling the liquid flow.
23. Off-gas was started to the gas gravitometer.
24. The furnace was allowed to come to thermal equilibrium and to a steady off-gas gravity.

Sampling and Data Logging

1. Flow of off-gas to the oxygen analyser was cut to allow a pressure of about 10 psig. to be built up in the sample bottles.
2. Sample bottles were replaced and flow resumed to the oxygen analyser.
3. A gas sample was obtained in the gas burette of the Orsat equipment and transferred to the acetylene analysis equipment.
4. Readings of temperatures, pressures and flow rates were recorded.
5. A sewer effluent sample was obtained for estimation of carbon content.

Shut Down

1. Liquid propane was shut off.
2. Pressure relief valve on the vaporizer was reset to about 10 psig.
3. Steam to the vaporizer was shut off.
4. Propane preheaters were shut off.
5. Pyrotacs were shut off: cutting off the oxygen, natural gas and propane solenoid valves, and opening the solenoid valve on the nitrogen purge.
6. Nitrogen was allowed to flow for a few minutes before shutting off the electrical system connected to the pyrotacs.
7. Air flow was reduced to about 8 SCFM to each burner.
8. Sampling equipment and surfactant spray were shut off.
9. The steam to the ejector was shut off and the valve on the off-gas line was fully opened.
10. When the furnace reached about 1000 $^{\circ}$F, the air and cooling water were shut off.

TABLE 3

OPERATING CONDITIONS

RUN NUMBER:	2-A	2-B	2-C	3-A	5-A,B	6-A	6-B
Premixed Gases to Burners							
Air:							
Temperature, °F	75	75	75	70	72	72	73
Flow Rates, SCFM							
Right Burner	17.05	17.13	17.13	17.2	14.55	17.51	17.68
Left Burner	17.02	17.13	17.13	17.1	14.20	17.46	17.68
Total Flow	34.07	34.26	34.36	34.3	28.75	34.97	35.24
Oxygen:							
Temperature, °F							
Flow Rates, SCFM							
Right Burner	NO OXYGEN USED IN THESE RUNS						
Left Burner							
Total Flow							
Natural Gas:							
Temperature, °F	78	78	78	72	72	70	70
Flow Rates, SCFM							
Right Burner	2.02	2.02	2.02	1.56	1.34	1.56	1.56
Left Burner	2.32	2.32	2.32	1.82	1.33	1.82	1.82
Total Flow	4.34	4.34	4.34	3.38	3.67	3.38	3.38
Nitrogen Purge, SCFM	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Propane System							
Vapor Flow, SCFM	6.31	7.73	7.73	9.81	7.20	7.38	9.72
Temperatures, °F							
Vaporizer	152	158	160	167	145	155	158
Interstage Preheat	564	567	553	555	562	572	570
Final Preheat	600	600	600	NA	590	590	580
Furnace-Quench System							
Temperatures, °F							
Right Burner Shell	340	350	345	400	345	340	300
Left Burner Shell	300	290	275	380	300	260	230
Furnace Wall*	2100	2010	1960	2010	1900	2070	1930
Quenched Gases	168	168	166	164	165	171	166
Quench Pressure, inches Hg abs.	26.8	27.0	27.2	27.0	27.5	28.1	28.1
Off-Gas System**							
Flow Rate, SCFM	43.94	43.82	43.82	43.8	39.2	43.62	55.57
Temperature, °F	130	128	126	124	119	125	118
Gravity	0.95	0.95	0.95	0.95	0.945	0.940	0.965
Oxygen Content, vol.%	1.7	3.2	3.4	0.7	1.9	1.0	2.1
Acetylene Content, vol.%	1.1	1.1	1.1	NA	NA	NA	NA

* Furnace wall temperature measured with an optical pyrometer.

** Off-gas:
- i. flow rates reported are calculated from orifice meter data;
- ii. gravity, oxygen content, and acetylene content are reported on a water free basis;
- iii. oxygen content obtained from Burell Oxygen Analyser;
- iv. acetylene content obtained by precipitation of silver acetylide from a solution of silver nitrate.

TABLE 3 (Cont'd)

OPERATING CONDITIONS

RUN NUMBER:	7-A	8-A	8-B	8-C	9-A,B	10-A
Premixed Gases to Burners						
Air:						
Temperature, °F	67	85	82	82	82	75
Flow Rates, SCFM						
Right Burner	23.3	16.80	11.60	11.0	12.2	15.70
Left Burner	24.1	16.81	11.68	11.0	11.6	15.67
Total Flow	47.40	33.41	23.28	22.0	23.8	31.37
Oxygen:						
Temperature, °F			30	30	60	53
Flow Rates, SCFM						
Right Burner	NOT	NOT	1.07	3.96	0.96	3.86
Left Burner	USED	USED	1.07	3.96	0.96	3.86
Total Flow			2.14	7.92	1.92	7.72
Natural Gas:						
Temperature, °F	60	NA	NA	NA	84	74
Flow Rates, SCFM						
Right Burner	2.53				1.34	3.15
Left Burner	2.48				1.33	3.12
Total Flow	5.01	3.57	3.57	5.8	2.67	6.27
Nitrogen Purge, SCFM	0.06	0.06	0.06	0.06	0.15	0.15
Propane System						
Vapor Flow, SCFM	11.24	3.79	3.80	6.9	7.95	8.83
Temperatures, °F						
Vaporizer	165	139	NA	NA	187	204
Interstage Preheat	576	NA	NA	NA	585	589
Final Preheat	590	NA	NA	NA	NA	NA
Furnace-Quench System						
Temperatures, °F						
Right Burner Shell	320	350	350	NA	345	350
Left Burner Shell	460	400	380	NA	325	300
Furnace Wall*	2450	1860	1930	NA	1890	2320
Quenched Gases	172	NA	NA	NA	182	186
Quench Pressure, inches Hg abs.	27.5	NA	NA	NA	27.6	27.2
Off-Gas System**						
Flow Rate, SCFM	60.9	39.87	33.1	NA	38.8	56.5
Temperature, °F	139	137	132	NA	129	148
Gravity	1.00	0.90	0.822	NA	0.887	0.785
Oxygen Content, vol.%	0.3	NA	NA	NA	1.2	NA
Acetylene Content, vol.%	NA	NA	NA	NA	NA	3.3

* Furnace wall temperature measured with an optical pyrometer.

** Off-gas:
- i. flow rates reported are calculated from orifice meter data;
- ii. gravity, oxygen content, and acetylene content are reported on a water free basis;
- iii. oxygen content obtained from Burell Oxygen Analyser;
- iv. acetylene content obtained by precipitation of silver acetylide from a solution of silver nitrate.

TABLE 3 (Cont'd)

OPERATING CONDITIONS

RUN NUMBER:	11-A	11-B	12-A	12-B	12-C	12-D,E
Premixed Gases to Burners						
Air:						
Temperature, $^{\circ}F$	81	81	82	82	82	82
Flow Rates, SCFM						
Right Burner	15.87	15.98	10.9	10.9	10.9	10.9
Left Burner	16.08	16.17	11.1	11.1	11.1	11.1
Total Flow	31.95	32.15	22.0	22.0	22.0	22.0
Oxygen:						
Temperature, $^{\circ}F$	50	50	NA	NA	NA	NA
Flow Rates, SCFM						
Right Burner	3.78	5.34	0.93	0.93	0.93	0.93
Left Burner	3.78	5.34	0.93	0.93	0.93	0.93
Total Flow	7.56	10.68	1.86	1.86	1.86	1.86
Natural Gas:						
Temperature, $^{\circ}F$	78	78	79	79	79	79
Flow Rates, SCFM						
Right Burner	2.99	4.22	1.46	1.46	1.46	1.46
Left Burner	3.29	4.28	1.45	1.45	1.45	1.45
Total Flow	6.28	8.50	2.91	2.91	2.91	2.91
Nitrogen Purge, SCFM	0.15	0.15	0.15	0.15	0.15	0.15
Propane System						
Vapor Flow, SCFM	11.27	11.20	1.91	2.89	3.62	4.73
Temperatures, $^{\circ}F$						
Vaporizer	213	216	91	131	156	163
Interstage Preheat	576	584	524	510	518	528
Final Preheat	NA	NA	NA	NA	NA	NA
Furnace-Quench System						
Temperatures, $^{\circ}F$						
Right Burner Shell	290	330	340	480	570	625
Left Burner Shell	260	280	360	420	540	610
Furnace Wall*	2140	2290	2680	2500	2720	2600
Quenched Gases	182	186	175	174	176	178
Quench Pressure, inches Hg abs.	27.7	27.8	27.7	28.0	28.1	27.3
Off-Gas System**						
Flow Rate, SCFM	67.8	72.4	26.1	27.0	28.3	27.3
Temperature, $^{\circ}F$	128	154	116	117	121	126
Gravity	0.785	0.767	0.875	0.840	0.870	0.97 - 0.94
Oxygen Content, vol.%	0.4	0.4	1.2	1.9	2.3	2.4
Acetylene Content, vol.%	3.3	3.3	0.3	1.0	1.3	1.7

* Furnace wall temperature measured with an optical pyrometer.

** Off-gas: i. flow rates reported are calculated from orifice meter data;
ii. gravity, oxygen content, and acetylene content are reported on a water free basis;
iii. oxygen content obtained from Burell Oxygen Analyser;
iv. acetylene content obtained by precipitation of silver acetylide from a solution of silver nitrate.

TABLE 3 (Cont'd)

OPERATING CONDITIONS

RUN NUMBER:	14-A	14-B	15-A	15-B	15-C	15-D
Premixed Gases to Burners						
Air:						
Temperature, °F	85	85	76	78	76	77
Flow Rates, SCFM						
Right Burner	15.9	16.7	16.2	16.2	16.2	16.2
Left Burner	15.7	15.7	15.7	15.7	15.7	15.7
Total Flow	31.6	32.4	32.0	32.0	32.0	32.0
Oxygen:						
Temperature, °F	70	77	70	70	70	70
Flow Rates, SCFM						
Right Burner	0.81	0.82	0.83	0.83	0.83	1.03
Left Burner	0.81	0.82	0.83	0.83	0.83	1.03
Total Flow	1.62	1.64	1.66	1.66	1.66	2.06
Natural Gas:						
Temperature, °F	76	76	75	75	75	75
Flow Rates, SCFM						
Right Burner	1.96	1.96	2.09	2.09	2.09	2.09
Left Burner	1.90	1.90	2.03	2.03	2.03	2.03
Total Flow	3.86	3.86	4.12	4.12	4.12	4.12
Nitrogen Purge, SCFM	0.15	0.15	0.15	0.15	0.15	0.15
Propane System						
Vapor Flow, SCFM	5.83	5.71	5.86	8.88	11.12	16.30
Temperatures, °F						
Vaporizer	154	180	160	173	168	135
Interstage Preheat	569	573	529	574	572	466
Final Preheat	665	719	676	674	660	563
Furnace-Quench System						
Temperatures, °F						
Right Burner Shell	310	460	390	420	500	540
Left Burner Shell	300	500	400	415	400	380
Furnace Wall*	1900	2590	NA	2560	2450	NA
Quenched Gases	NA	NA	177	174	174	174
Quench Pressure, inches Hg abs.	26.6	27.6	27.9	27.8	27.3	27.7
Off-Gas System**						
Flow Rate, SCFM	42.8	41.0	42.2	---Pressure Taps Plugged ---		
Temperature, °F	74	75	69	70	68	69
Gravity	0.865	0.915	0.877	0.910	0.940	0.960
Oxygen Content, vol.%	NA	NA	0	0	0	0
Acetylene Content, vol.%	1.0	1.0	1.7	1.5	1.3	1.4

* Furnace wall temperature measured with an optical pyrometer.

** Off-gas:
- i. flow rates reported are calculated from orifice meter data;
- ii. gravity, oxygen content, and acetylene content are reported on a water free basis;
- iii. oxygen content obtained from Burell Oxygen Analyser;
- iv. acetylene content obtained by precipitation of silver acetylide from a solution of silver nitrate.

SAMPLE ANALYSIS

During each run several routine analyses were carried out to maintain a check on the stability of operation. Continuous sampling and analysis of the off-gas for oxygen content was possible with a Burell Oxygen Analyser. The off-gas was also sampled and the gravity measured on a continuous basis, by an Arcco Gas Gravitometer.

Routine checks on carbon dioxide content of the off-gas were attempted using an Orsat Unit. This test was, however, abandoned since the time involved made it impossible to maintain a continuous check on operating conditions of the furnace.

During several of the runs, the off-gas was analysed for acetylene on a spot sample basis. Acetylene content was obtained by precipitation of silver acetylide from a solution of silver nitrate, and back titration using sodium hydroxide.

Detailed analysis of off-gas samples was made using gas chromatography by the Research Council of Alberta. These samples were collected, under a positive pressure of about 5 psi., in glass sample bottles. Ethane, carbon dioxide, ethylene, propane and acetylene were separated using a silica gel column with helium as the carrier gas. A silica gel column was also used, with nitrogen as the carrier gas, to determine hydrogen content. A Linde Sieve, with helium, was used to separate oxygen, nitrogen, methane and carbon monoxide. Proplyene and propane were determined using a tri-iso-butylene column with helium.

Samples were collected and held, at the Research Council, until several samples were on hand. By doing this it was possible to limit the number of column changes required. A portion of each available sample was run through one particular column before the next column was installed.

This method of handling the samples was deterimental to the results of the analyses. All of the samples were obtained with a positive pressure of approximately 5 psi. With the long storage time (in some cases up to two weeks before a complete analysis was made) many of the samples lost this positive pressure through leakage. In order to obtain a portion of the gas from the depressurized samples, it was necessary to pressurize the containers by mercury injection. This often resulted in considerable contamination with air.

In addition to the loss in pressure, several other effects could have resulted from long storage periods. Hydrogen presumably could diffuse past the stopcocks in the sample containers and escape. No direct check on this occurrence was made, however, attempts at making a material balance around the furnace indicated, in some cases, a low hydrogen analysis.

Ethylene and acetylene may have been adsorbed by the stopcock grease. The loss of acetylene was shown by the fact that on the spot acetylene checks, made during a run, gave up to 3 per cent, yet the results from duplicate samples sent to the Research Council showed no acetylene present.

Other sources of errors were possible through the operating methods and limitations of the Chromatography unit. Temperatures used during the analyses were too low to obtain sharp, well defined peaks. In several cases the peaks were flattened to the point where there was overlapping on successive peaks. The use of higher temperatures would have given sharper peaks and would have reduced or eliminated the interference of peaks. This interference was particularly noticeable with acetylene and propane; with acetylene appearing as a small shoulder on the propane peak.

Low temperatures also resulted in base line drift in some of the analyses. Many of the components not separated by a particular column would be elutriated in close sequence, resulting in a very large peak. In some instances these large peaks were not sharp and resulted in a long trailing edge at some distance above the base line (but gradually moving back towards the base line). The peaks formed by components, separated by the column, were then measured from a drifting base line. In addition, the reliability of the peaks measured was in doubt as compared to pure components. The drifting base line indicates a gradual elutriation of other components from the column. Thus, the peaks produced were not for pure components, but for the components mixed with the material gradually being released from the column. Higher column temperatures would have eliminated or, at least, reduced this condition by giving more complete and sharper separation of the components causing the base line drift. This base line drift was very prominent with the separation of propane and propylene by the tri-iso-butylene column.

The sensitivity of the detector cell was not altered during the run of a sample on a column. Instead, the sensitivity was set to give a reasonable chart reading for the component present in the largest amount.

With no change in sensitivity made for the peaks of components present in lesser amounts, the resulting peaks were often very small and shallow. (The shallowness was probably caused by the low column temperatures.) In some cases the peaks were so small that the recorder pen width could have conceivably produced an error in measuring peak height of as much as 50 per cent or more.

Many of the analyses received did not total up to 100 per cent, making it necessary to adjust the reported values in some manner. The adjustments required were not clear cut in nature due to the use of four column-carrier gas combinations used to obtain a complete analyses. Any group of components could have been in error, with no indication as to which. In some cases, air contamination was indicated by excess oxygen and nitrogen contents.

All of the analyses received from the Research Council reported oxygen content higher than indicated by the oxygen analyser. This error was assumed to be caused, in part, by the small amount of argon present in the air used to support combustion. Argon was elutriated with oxygen from the Linde Sieve. Checks made, using material balances, confirmed this and made it possible to make the necessary corrections. In making these adjustments, the oxygen content indicated by the oxygen analyser was assumed to be correct.

With the corrected oxygen content and the calculated argon content, the reported analysis could be checked for air contamination. A nitrogen balance was also used to check for air contamination. In all cases where air contamination was found, the methane and carbon dioxide contents were adjusted. By assuming air contamination of the whole sample, with the same amount as indicated by the oxygen and nitrogen contents, the remaining components could be adjusted. This assumption could not be checked, and with several samples the adjustments were not completely satisfactory. Variations in the amount of air contaminating the different portions of the samples, used in obtaining the complete analysis, could not be checked for.

Hydrogen losses by diffusion out of the sample containers and losses of unsaturates by adsorption onto the stopcock grease could not be determined or adjusted for. No evaluation or adjustments were possible for errors resulting from limitations of the chromatography unit or for errors caused by operation techniques.

For the most part, adjustments made to the analyses were of a trial and error nature, with the use of the adjusted values in a material balance serving as a guide. Losses of hydrogen and oxygen in the material balance were adjusted in approximately the proportions required for water (since water formed in the combustion was lost in quenching and cooling of the gases). Trial adjustments were made using material balances on individual elements.

Table 4 gives the off-gas analyses as obtained from the Research Council. Copies of typical charts from the chromatography analysis of the off-gas are presented in the appendix.

TABLE 4

OFF-GAS ANALYSES AS REPORTED BY THE RESEARCH COUNCIL OF ALBERTA

RUN NUMBER:	2-A	2-B	2-C	3-A	3-B*	5-A	5-B	6-A	6-B
Oxygen and Argon	3.2	4.3	4.6	1.3	1.3	2.8	3.1	6.1	5.1
Nitrogen	60.0	58.2	59.0	58.2	58.2	59.2	60.1	63.6	60.0
Carbon Monoxide	7.2	6.7	6.3	7.6	7.7	6.6	6.8	6.2	6.4
Methane	4.2	4.5	4.3	1.8	1.8	4.7	4.7	4.7	4.9
Hydrogen	8.8	7.5	7.4	8.3	9.0	8.4	8.4	7.5	8.3
Ethane	0.7	1.1	1.0	1.1	0.7	1.0	0.7	0.7	0.9
Ethylene	2.3	2.3	2.2	1.6	1.2	3.1	2.7	2.7	2.6
Carbon Dioxide	3.7	3.7	3.6	4.0	3.0	4.3	3.8	4.3	3.7
Propane	6.2	9.9	9.8	12.8	12.5	9.2	8.6	6.1	11.1
Propylene	-	-	-	0.39	0.39	0.68	0.65	0.57	0.65
Acetylene	-	-	-	-	-	-	-	-	-
TOTAL	96.3	98.2	98.2	97.99	95.79	99.98	99.55	102.47	103.65

Note: No samples available for Run Number 1.

Samples for Run Number 4 were contaminated with large amounts of air.

* Duplicate sample.

TABLE 4 (Cont'd)

OFF-GAS ANALYSES AS REPORTED BY THE RESEARCH COUNCIL OF ALBERTA

RUN NUMBER:	7-A	8-A	8-B	8-C	9-A	9-B	10-A	11-A	11-B
Oxygen and Argon	12.6	3.4	3.9	0.8	4.6	4.3	0.8	1.0	1.6
Nitrogen	70.5	63.8	55.2	38.1	54.8	51.5	40.4	39.8	37.1
Carbon Monoxide	2.5	9.6	12.5	20.6	9.4	9.4	17.8	16.0	18.4
Methane	1.9	6.4	6.1	4.0	6.9	7.0	4.3	7.2	4.9
Hydrogen	1.8	5.8	6.2	27.1	4.9	8.1	25.4	23.5	26.8
Ethane	0.8	0.3	0.1	0.1	0.2	0.3	0.2	0.2	0.2
Ethylene	1.7	2.7	2.3	1.5	1.9	4.0	2.3	4.1	2.4
Carbon Dioxide	4.2	3.9	4.0	4.5	1.4	3.0	4.4	4.5	4.2
Propane	9.3	1.2	0.8	1.9	6.3	6.2	3.8	3.3	3.7
Propylene	0.37	0.27	0.18	0.28	1.2	1.2	0.4	0.33	0.39
Acetylene	-	trace	2.50	2.1	-	-	1.0	2.5	1.4
TOTAL	105.67	97.37	93.78	100.98	91.6	95.0	100.8	102.43	101.09

TABLE 4 (Cont'd)

OFF-GAS ANALYSES AS REPORTED BY THE RESEARCH COUNCIL OF ALBERTA

RUN NUMBER:	12-A	12-B	12-C	12-D	12-E	14-Ar	14-C	14-Cr
Oxygen and Argon	1.1	1.3	2.9	2.6	0.9	1.1	1.1	1.2
Nitrogen	61.8	56.6	57.6	60.3	58.5	55.2	56.7	60.9
Carbon Monoxide	14.8	15.0	12.5	8.3	7.2	11.0	11.4	10.8
Methane	2.0	2.9	3.1	3.3	4.2	6.9	2.3	2.7
Hydrogen	15.4	16.9	14.2	8.6	10.1	16.6	13.7	12.6
Ethane	-	0.1	0.2	0.3	0.4	0.2	0.2	0.3
Ethylene	0.8	1.3	1.8	2.5	3.7	4.0	1.9	2.3
Carbon Dioxide	5.4	4.5	3.5	6.0	8.1	-	4.7	-
Propane	1.7	3.2	3.8	6.8	7.2	2.2	6.9	7.7
Propylene	0.15	0.26	0.31	0.45	0.63	0.3	0.5	0.5
Acetylene	-	-	-	-	-	2.5	-	-
TOTAL	103.15	102.06	99.91	99.15	100.93	100.0	99.4	99.0

Note: No samples available for Run Number 13.

Run numbers followed by an "r" indicate samples which were scrubbed with Ascarite to remove carbon dioxide.

TABLE 4 (Cont'd)

OFF-GAS ANALYSES AS REPORTED BY THE RESEARCH COUNCIL OF ALBERTA

RUN NUMBER:	15-A	15-Ar	15-B	15-Br	15-C	15-Cr	15-D	15-Dr
Oxygen and Argon	5.0	1.0	1.0	1.2	1.0	1.0	11.3	5.4
Nitrogen	59.0	56.9	52.3	54.6	48.8	51.3	60.0	51.9
Carbon Monoxide	10.0	12.4	12.7	12.7	11.2	11.4	6.2	9.2
Methane	3.0	4.0	3.6	3.7	3.5	3.7	1.9	2.6
Hydrogen	15.6	16.7	15.4	16.1	16.3	17.2	12.0	15.6
Ethane	0.1	0.3	0.4	0.3	0.4	0.4	0.1	0.1
Ethylene	1.3	3.2	3.7	1.6	4.3	3.1	0.5	0.3
Carbon Dioxide	2.5	-	4.1	0.1	3.6	-	0.9	0.1
Propane	1.8	5.1	8.1	4.2	11.4	12.0	4.8	7.0
Propylene	0.1	0.4	0.9	0.4	0.4	0.8	0.3	0.3
Acetylene	1.4	-	-	-	-	-	-	-
TOTAL	99.8	100.0	102.2	94.9	100.9	100.9	98.0	92.5

Note: Run numbers followed by an "r" indicate duplicate samples which were scrubbed with Ascarite to remove carbon dioxide.

RESULTS AND OBSERVATIONS

Original plans were to operate the reactor at two temperature levels. A low temperature level of approximately 1600 °F was planned for procucing ethylene and a high level of 2300 °F was planned for acetylene production.

The primary runs were made using a six inch spacing between the burner blocks. (At this spacing it was hoped to produce conditions for ethylene formation.) With no propane feed entering the furnace it was possible to maintain satisfactory operation of the burners. Introduction of propane at low flow rates had no noticeable effect on combustion or operation of the burners. Observation of the reaction zone indicated total destruction of the propane to carbon black.

Increased quantities of propane created a pressure build up within the furnace. Presumably this was caused by rapid cracking of the propane. This pressure blocked the incoming feed and forced the flame into the burner ports. Dissipation of the pressure allowed the flame to advance out of the burner ports and the propane flow to resume. The overall effect was to establish a resonance which magnified the disturbances and eventually combustion would deteriorate to the point where the burners would blow out. (The gradual deterioration of combustion was evident from the increasing amounts of oxygen in the off-gas.)

These fluctuations were first thought to originate within the propane vaporizer since good burner operation was possible with no propane entering the reaction zone. As an attempt to eliminate the unsteady operation, a pressure regulator and a critical flow orifice were installed in the propane vapor line. In spite of these additions fluctuations persisted, however, it was possible to operate the furnace with a limited amount of propane feed.

At this point it was noticed that the off-gas cooling tower had a tendency to flood. Since this was another possible source of fluctuations, the furnace was operated with only the primary quench relied upon for cooling. This improved the operation of the furnace but it was still impossible to operate with feed to fuel ratios of one or greater.

Any attempts to operate the furnace at the low temperature level failed through gradual deterioration of combustion. High temperatures were attained using very low propane feed rates, however analysis of the off-gas showed that complete pyrolysis to carbon and hydrogen was all that was

possible. The high oxygen content of the off-gas indicated the poor combustion present. Radiation losses to the quench were also thought to be high, adding to the poor combustion.

With these effects present it was felt that a smaller spacing between the burners would help in stabilizing the furnace. Accordingly, the burners were positioned at three inches apart.

Operation of the furnace with fuel to feed ratios as high as three was possible with the burners set at the three inch spacing. Temperature control was possible only to a limited extent as the final reactor temperature depended primarily upon the manner in which the feed was introduced. If the feed rate was slowly increased to a desired level, temperatures were maintained in the order of 2300 °F and higher. Temperature drops occurred upon increasing feed rates, but the original level was soon attained. Immediate introduction of the feed at the desired rate caused the temperature to drop to about 1900 °F, where it would remain until the feed rate was changed. Increasing the feed rate caused further reductions in temperature and the furnace would eventually become unstable and blow out.

During the runs at the low temperatures, partial combustion of the propane occurred. This was evident by considerable atmospheric contamination by the effluent water. Many of the oxygenated compounds were dissolved in the cooling water and later released in the seal pot leading to the sewer.

During the runs where high temperatures were maintained, much of he propane reacted went to carbon and hydrogen, with only small amounts going to ethylene and acetylene. Some of the propane may have been consumed by combustion, however the majority of the propane passed through the furnace unreacted.

Mixing within the furnace was very poor. The maximum Reynolds Number attained was in the order of about 1000, indicating very little mixing due to turbulence. Observations through the pyrometer port on the furnace further indicated the poor mixing within the reaction zone. With the carbon produced in the reaction zone, it was possible to observe the flow patterns developed. Originally it was thought that the combustion gases coming from the sides and the feed entering from the top would promote a reasonable amount of mixing. The apparent flow pattern indicated that the combustion products moved out from the burners and curved down towards the quench, with the feed channeling

down through the center. At the interface between the gas streams, some mixing was evident. Poor mixing was further verified by the large percentage of propane coming through the furnace uncracked. In some of the runs, up to 75 per cent of the propane remained unreacted. During one particular run, a thin walled thermocouple well was installed within the quench tube. About 25 per cent of the propane was reacted during this run, yet the stainless steel well was melted and burned. This indicated that temperatures ranged from about 3000 °F to less than 1200 °F within the reaction zone.

When using the six inch spacing, the burners were cooled by water coils cemented to the shells with a special cement having a high thermal conductivity. These coils maintained the temperature in the burner shell at about 150 °F. When the spacing was reduced, the burners were replaced without the cooling coils. This allowed the shell temperature to reach as high as 700 °F with no noticeable detrimental effects. However, it was found that if the temperature of the shell reached 600 °F or greater the ratio of carbon monoxide to carbon dioxide in the off-gas was reduced even though the remaining conditions within the furnace were fairly constant. This indicated that some preheating of the fuel mixture may have helped combustion.

High temperatures were a source of trouble in connection with the refractory materials. The bricks lining the reaction zone, and in intimate contact with the high temperatures were a commercial brick designed to withstand temperatures up to 3200 °F. These bricks withstood the temperatures developed with no melting, however there was considerable spalling and shrinkage at points in direct contact with the hot combustion gases. Some breakage of large sections of brick was also encountered. It was found that thin sections, or small blocks cut in an interlocking pattern, withstood the thermal stresses much more satisfactorily than complete bricks.

Immediately above the reaction zone, a large section was insulated with refractory brick to protect the top plate of the furnace shell. These bricks were first installed as a solid block made up of several bricks cemented together. Cementing of these bricks into a solid unit was later abandoned as the high temperatures caused the refractory cement to melt and run down in the reaction zone. This cement was specified by the manufacturer to withstand temperatures as high as 3000 °F.

High temperatures also had serious detrimental effects on the burner blocks. Repeated heating and cooling eventually caused some spalling and the formation of many hair line cracks. One burner failed completely and caused a flow of burning gas to be deflected back towards the cast iron shell. This caused extremely high temperatures within the shell and a large section of one side was destroyed by melting and oxidation of the metal.

Carbon formation was a problem, causing considerable plugging of the off-gas system. Although a surfactant was used to remove most of the carbon, the off-gas orifice meter was continually coated with carbon. Because of this, measured off-gas flow rates were seldom reliable. Difficulties encountered with sample analysis have been outlined in a previous section.

The adjusted off-gas analyses, flow rates and gravities are presented in Table 5.

TABLE 5

ADJUSTED OFF-GAS ANALYSES, GRAVITIES AND FLOW RATES

RUN NUMBER:	2-A	2-B	2-C	3-A,B	5-A,B	6-A	6-B
Oxygen and Argon	2.32	3.57	3.85	0.75	1.90	1.41	2.70
Nitrogen	58.17	56.10	56.89	59.28	59.10	59.77	55.40
Carbon Monoxide	7.41	6.82	6.39	8.08	7.30	7.90	7.10
Methane	4.32	4.58	4.36	1.91	5.00	5.98	5.36
Hydrogen	10.68	9.70	8.78	8.82	9.00	7.50	8.30
Ethane	0.74	1.08	1.03	1.17	0.80	0.70	0.96
Ethylene	2.41	2.26	2.26	1.70	2.90	2.69	2.80
Carbon Dioxide	3.94	3.62	3.69	4.25	4.10	4.31	3.96
Propane	8.08	10.52	11.09	13.61	9.20	8.48	12.14
Propylene	0.55	0.67	0.59	0.43	0.70	0.76	0.64
Acetylene	1.38	1.08	1.07	-	-	0.50	0.54
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Off-Gas Gravity							
Calculated	0.927	0.948	0.960	0.965	0.950	0.952	0.968
Measured	-	-	-	-	0.945	0.940	0.965
Off-Gas Flow, SCFM							
Calculated	45.95	47.86	47.37	48.76	40.58	46.01	49.99
Measured	43.94	43.82	43.82	43.80	39.20	43.62	47.70

TABLE 5 (Cont'd)

ADJUSTED OFF-GAS ANALYSES, GRAVITIES AND FLOW RATES

RUN NUMBER:	7-A	8-A	8-B	8-C	9-A,B	10-A	11-A	11-B
Oxygen and Argon	0.77	2.30	0.93	0.73	1.66	0.77	0.86	1.54
Nitrogen	61.00	66.50	53.32	35.25	47.42	39.05	37.32	35.61
Carbon Monoxide	5.60	9.60	16.55	19.12	10.08	17.19	15.40	17.66
Methane	4.26	6.40	8.08	3.71	7.50	4.15	6.91	4.70
Hydrogen	5.40	6.32	8.22	27.10	13.32	24.54	22.71	25.72
Ethane	1.04	0.33	0.13	0.12	0.33	0.19	0.19	0.19
Ethylene	2.21	2.94	3.07	1.73	4.29	2.22	3.96	2.30
Carbon Dioxide	5.45	3.90	5.32	5.16	3.21	4.25	4.35	4.03
Propane	12.00	1.31	1.07	4.08	8.29	3.67	4.68	5.56
Propylene	0.47	0.29	0.24	0.60	1.36	0.39	0.43	0.58
Acetylene	1.80	0.11	3.07	2.40	2.54	3.58	3.19	2.11
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Off-Gas Gravity								
Calculated	1.000	0.903	0.825	0.755	0.889	0.776	0.787	0.776
Measured	1.000	0.900	0.822	0.763	0.887	0.785	0.785	0.765
Off-Gas Flow, SCFM								
Calculated	60.90	41.77	35.80	50.40	39.80	63.72	67.90	72.40
Measured	60.90	34.87	33.10	NA	38.8	56.5	67.8	72.4

TABLE 5 (Cont'd)

ADJUSTED OFF-GAS ANALYSES, GRAVITIES AND FLOW RATES

RUN NUMBER:	12-A	12-B	12-C	12-D	12-E	14-A	14-C
Oxygen and Argon	1.06	0.94	1.00	1.05	1.01	1.05	1.10
Nitrogen	59.68	54.54	54.23	57.20	55.26	52.60	56.70
Carbon Monoxide	14.29	14.78	13.72	8.65	6.80	10.50	11.40
Methane	1.92	2.86	3.41	3.46	3.97	6.57	2.30
Hydrogen	14.88	16.85	15.60	8.95	9.52	15.83	13.70
Ethane	0.10	0.09	0.22	0.30	0.38	0.20	0.30
Ethylene	0.79	1.29	1.97	2.63	3.49	3.75	2.30
Carbon Dioxide	5.22	4.33	3.85	6.28	7.66	4.70	4.70
Propane	1.65	3.10	4.25	9.15	8.32	2.20	5.80
Propylene	0.14	0.25	0.34	0.59	0.73	0.30	0.50
Acetylene	0.27	0.97	1.41	1.74	2.86	2.30	1.20
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Off-Gas Gravity							
Calculated	0.858	0.851	0.860	0.965	0.960	0.852	0.898
Measured	0.875	0.840	0.870	0.970	0.940	0.865	0.915
Off-Gas Flow, SCFM							
Calculated	29.13	31.87	32.00	30.40	31.48	48.16	44.73
Measured	26.1	27.0	28.3	27.3	27.3	48.2	41.0

TABLE 5 (Cont'd)

ADJUSTED OFF-GAS ANALYSES, GRAVITIES AND FLOW RATES

RUN NUMBER:	15-A	15-B	15-C	15-D
Oxygen and Argon	0.86	0.82	0.75	0.71
Nitrogen	53.41	49.10	46.90	41.62
Carbon Monoxide	11.78	11.52	10.56	11.54
Methane	3.81	3.41	3.41	3.25
Hydrogen	15.21	15.85	15.66	14.89
Ethane	0.31	0.37	0.39	0.38
Ethylene	3.27	3.47	4.13	1.90
Carbon Dioxide	4.36	3.84	3.75	3.45
Propane	4.94	9.25	12.61	19.96
Propylene	0.39	0.89	0.40	0.82
Acetylene	1.66	1.48	1.44	1.48
TOTAL	100.00	100.00	100.00	100.00
Off-Gas Gravity				
Calculated	0.872	0.890	0.905	0.955
Measured	0.877	0.910	0.940	0.960
Off-Gas Flow, SCFM				
Calculated	47.22	51.43	53.85	60.60
Measured	orifice meter plugged			

DISCUSSION

From the results and observations of the experimental runs and the general operation of the reactor several problems were evident:

i. The materials of construction used in the reactor were not suited to the severe temperature cycles encountered in short term runs;

ii. No appreciable effect of radiation as a means of transferring heat to the feed gas was evident. Radiation heat losses to the quench section of the reactor were, however, an important factor in burner stabilization;

iii. Only limited mixing of the combustion gases and the propane feed was obtained. The core of the reactor was propane with layers of various compositions approaching straight combustion gases at the walls of the reactor. Residence time, composition and temperature were different for each zone in the reactor;

iv. Considerable amounts of carbon monoxide and carbon black were formed and accounted for a high percentage of the propane reacted.

Regarding the first two problems, materials are available which would be suitable for the reactor. A program of investigating various commercially available steels and refractories would be necessary to develop a full scale reactor. The burner should be designed to operate at as high a temperature as possible with preheated and premixed fuel. The burner ports should minimize radiation losses in order to stabilize the combustion. A burner design which achieves rapid and stable combustion irregardless of conditions prevailing at the burner outlet is certainly possible. This type of burner would make possible a pyrolysis reaction system which could have advantages over present commercial reactors.

To correlate the results or to compare them with other processes requires some basis for calculation. Equilibrium equations and material balances could be used combined with the concept of approach to equilibrium.(20,21) The approach to equilibrium is explained as the ratio of K'/K where K is the equilibrium constant; $\ln K = -\Delta F^{o}/RT$, and K' is the actual ratio of activities of the components in the reaction considered. The necessary number of approach to equilibrium ratios could be determined to define the system, however, the mixing problem makes it impossible to know what ratio of components are subjected to a given temperature and contact time. No comprehensible mathematical system could be devised without using many arbitrary accumptions

about conditions in the reactor. The equilibrium involving the formation of carbon has an approach ratio less than 0.001 and no reliable correlation could be obtained so that a value of this very important quantity would have to be assumed. Kinetics are equally inapplicable due to the complexity of the reactor.

Reaction mechanism combined with data from similar commercial and experimental processes provides the best means of interpreting the reaction performace. The mechanism for hydrocarbon pyrolysis involves initial cracking to methane, ethane and ethylene with subsequent reaction as follows:

$$2\ CH_4 \longrightarrow C_2H_6 + H_2$$
$$C_2H_6 \longrightarrow C_2H_4 + H_2$$
$$C_2H_4 \longrightarrow C_2H_2 + H_2$$
$$C_2H_2 \longrightarrow 2\ C + H_2$$

The actual mechanism is primarily free radical for the first two reactions, while the third is a molecular rearrangement. These reactions are approximately first order reactions. The formation of carbon is some form of polymerization of second order or higher.

The mechanism for partial combustion involves initial rapid reaction of the oxygen with part of the hydrocarbon to form CO_2 and H_2O in the ratio of C/H_2 in the fuel, followed by reforming of CO_2 and H_2O with the remaining hydrocarbon to form CO and H_2.(22,23,24)

The experimental process was as follows:

a. Burning a fuel gas to CO_2 and H_2O;

b. Mixing with a preheated feed gas giving reforming and pyrolysis reactions;

c. Quenching to stop the reaction and prevent the formation of carbon black.

The partial combustion type of reactor like the Sachsse process is as follows:

i. Mixing a preheated feed gas with just enough preheated oxygen to supply the heat for the reaction. Mixing completed during the preignition period;

ii. Initial rapid combustion of part of the feed gas with the oxygen to form CO_2 and H_2O;

iii. Subsequent reforming of the combustion gases and pyrolysis of the remaining feed gas;

iv. Quenching.

Since there is a preignition period before the initial combustion reaction, the gases have sufficient time to reach a homogeneous composition throughout the reactor. As conditions are homogeneous in the Sachsse reaction, equilibrium or kinetic calculations can be made with confidence. The data from partial combustion reactions (8,9,10) provide a basis for comparing the data of the other reaction schemes, since they provide information about relative rates of reforming and pyrolysis reactions and carbon forming reactions. It was also evident that the reaction scheme studied would merely become the same as a partial combustion process if a reactor could be designed to give instantaneous mixing.

The data shows the following points:

i. Reforming of CO_2 to CO is just as fast as the pyrolysis reactions;

ii. Carbon formation depends on acetylene concentration, being negligible where acetylene is present in low concentrations, and approaching a rate equal to the pyrolysis where conditions favor acetylene formation or whenever acetylene has a partial pressure of 0.04 atmospheres or greater;

iii. Reforming of H_2O to CO and H_2 is negligible. Therefore the water in the off-gas can be calculate from the oxygen feed and the stoichiometric equation for the combustion of the fuel. This applies equally well to reactions where the combustion gases are mixed with a hydrocarbon feed and where large concentration and temperature gradients exist.

One experimental process burned hydrogen for fuel(25) and used steam dilution for temperature control. One run used 1270 moles of steam at 3200 °F to pyrolize 100 moles of normal butane. The off gas temperature was 1600 °F and eight moles of CO and four moles of CO_2 were present in 316 moles of off-gas, dry basis. Assuming that these products were produced by reforming water gives a conversion of 1.3 percent and an approach to equilibrium ratio for the reaction:

$$CH_4 + H_2O \longrightarrow CO + 6H_2$$

of 3×10^{-9}.

The reaction:

$$CO + H_2O \longrightarrow CO_2 + H_2$$

was very close to equilibrium with a ratio of about 0.15. These small amounts

of CO and CO_2 could possibly have been impurities in the dilution steam. It was evident that water was practically inert under these conditions. Therefore the use of steam or any inert heat carrier gas would eliminate the problem of reforming reactions. The effect of steam dilution also eliminated carbon black formation, but this desirable effect depends upon the degree of mixing in the reactor. Other data at similar steam to feed gas ratios show that carbon black was formed.

Thus the only compatible explaination for the presence of paraffin hydrocarbons, carbon dioxide, ethylene, acetylene and carbon black in the off-gas was that several zones with varying compositions, temperatures and residence times existed in the reactor due to incomplete mixing. This condition, caused by incomplete mixing, was evident in all the data on processes similar to the experimental reactor and gave a consistent basis for comparison. Also assuming water was inert and calculating the water content of the off-gas from the oxygen in the fuel gave good material balance checks.

It may be concluded that the process studied would have advantages if hydrogen were used as a fuel. Various arrangements could be devised to generate hydrogen and the reduction of CO and CO_2 in the off-gas to minor quantities would simplify the separation of the products. Inert diluents can also be used to advantage in this type of process.

The technical problem to be resolved however, is how to rapidly mix the heat carrier with the feed. Possibly the use of fluidized solids may offer advantages.

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25. C. Paddrani, G. Salvi and A. Fuimara, Kinetic Aspects of Partial Oxidation of Methane by Oxygen and Air on Catalysts, Fourth World Petroleum Congress, Section iv/B, Paper No. 5

26. H. Krekeler, R. Wirtz, and N. Pechtold, Fundamental Relationships in the Pyrolysis of Hydrocarbons to Acetylene and Ethylene, Fifth World Petroleum Congress, Section iv, Paper No. 5

APPENDIX "A"

Following are copies of the calculations required to determine the air, oxygen, natural gas, propane, and off-gas flow rates. Copies of the gas gravitometer and oxygen analyser charts are also given.

AIR FLOW RATES (Orifice)

	Right	Left
Flowing Temperature, T °R	541	541
Barometric Pressure, in. Hg	27.77	27.77
Flowing Pressure, in. Hg ga.	1.80	2.20
" " , in. Hg abs. (P_f)	29.57	29.97
Pressure Drop, (h_w) cm. H_2O	25.1	25.4
h_w/P_f	0.84	0.84
$0.00848\, h_w/P_f$	0.007	0.007
$\underline{Y} = 1 - 0.00848\, h_w/P_f$	0.993	0.993
$h_w(P_f)$	742.2	761.2
$\sqrt{h_w(P_f)}$	27.24	27.59
$0.1151/\sqrt{h_w(P_f)}$	0.004	0.004
$\underline{F_r} = 1 + 0.1151/\sqrt{h_w(P_f)}$	1.004	1.004
$h_w(P_f)/T_f$	1.372	1.401
$\sqrt{h_w(P_f)/T_f}$	1.171	1.186
$Q = 13.558\, Y F_r \sqrt{h_w(P_f)/T_f}$, SCFM	15.83	16.03

OXYGEN FLOW RATE

Rotameters:

$$Q = CH\sqrt{\frac{P_f}{G\,T_f\,Z}}$$

To Burner:	Right	Left
Scale Reading, H	35	35
Coefficient, C	0.675	0.675

Flowing Pressure, P_f = 14.5 psia.

Flowing Temperature, T_f = 510°R

Oxygen:

= 99.5 % pure
- assume 0.5 % Argon

Gravity, G = 1.105 (Air = 1.000)

Compressability, Z = 1.00 (assumed)

Flow:

$$\text{Right Flow} = \text{Left Flow} = 0.675(35)\sqrt{\frac{14.5}{1.105(510)}} = 3.78 \text{ SCFM.}$$

Total Flow = 7.56 SCFM (at 60°F & 14.4 psia.)

Oxygen = 7.52 SCFM

Argon = 0.04 SCFM

NATURAL GAS FLOW RATES

Displacement Meter:

Initial Reading = 4193 ft^3

Final Reading = 4316 ft^3

Total Flow = 123 ft^3 at meter conditions

Total Time = 25.6 minutes

Flowing Pressure = 39.67 in. Hg. abs.

Flowing Temperature = 538 °F

Total Flow:

$$\frac{123\,(39.67)\,14.7\,(520)}{25.6\,(29.92)\,14.4\,(538)} = 6.28 \text{ SCFM} \quad (14.4/60)$$

Rotameters:

	Right	Left
Scale Reading	6.6	1.4
Coefficient	0.148	0.770

$$\frac{\text{Right}}{\text{Left}} = \frac{6.6\,(0.148)}{1.4\,(0.770)} = 0.907$$

$$\underline{\text{Left Flow}} = \frac{6.28}{1.907} = \underline{3.29 \text{ SCFM}}$$

$$\underline{\text{Right Flow}} = 6.28 - 3.29 = \underline{2.99 \text{ SCFM}}$$

PROPANE FLOW RATE

Critical Flow Orifice:

$$Q = \frac{C\,P_f}{\sqrt{G\,T_f\,Z}}$$

Propane:

93 °/∘ C_3H_8 (From Imperial Oil Gas Plant
6 °/∘ C_2H_6 at Redwater)
1 °/∘ C_4H_{10}

Gravity, G = 1.495
Compressability, Z = 1.0 (assumed)

Flow:

Flowing Pressure, P_f = 50.64 psia.
Flowing Temperature, T_f = 676 °R
Coefficient, C = 7.06 (from calibration)

$$\text{Flow, } Q = \frac{7.06(50.64)}{\sqrt{1.495(676)}} = \underline{11.27 \text{ SCFM}}$$

OFF-GAS FLOW RATE (Orifice)

Barometric Pressure, in. Hg	27.77
Flowing Pressure, in. Hg ga.	-0.70
" " , in. Hg abs.	27.07

Flowing Temperature, $t_f = 128\,°F$, $T_f = 588°R$

Dry Gas Gravity, $G_d = 0.785$

Vapor Pressure H_2O at t_f, $P_w = 4.33$ in. Hg abs.

$$\frac{P_w}{P_f} = 0.16\,, \quad 0.62\frac{P_w}{P_f} = 0.099\,, \quad 1 - \frac{P_w}{P_f} = 0.84\,, \quad G_d\left(1 - \frac{P_w}{P_f}\right) = 0.659$$

Wet Gas Gravity, $G_w = 0.62\frac{P_w}{P_f} + G_d\left(1 - \frac{P_w}{P_f}\right) = 0.758$

Pressure Drop, h_w cm. H_2O = 36.1

$$Y = 1 - 0.00934\frac{h_w}{P_f} = 0.9875$$

$$h_w(P_f) = 997\,, \quad \sqrt{h_w(P_f)} = 31.24$$

$$F_r = 1 + 0.0882 \Big/ \sqrt{h_w(P_f)} = 1.0028$$

$$\frac{h_w P_f}{G_w T_f} = 2.193\,, \quad \sqrt{\frac{h_w P_f}{G_w T_f}} = 1.481$$

$$Q_w = 55.307\, Y\, F_r \sqrt{\frac{h_w P_f}{G_w T_f}} = 80.8 \text{ SCFM (Wet)}$$

$$Q_d = Q_w\left(1 - \frac{P_w}{P_f}\right) = \underline{67.8 \text{ SCFM}} \text{ (Dry)}$$

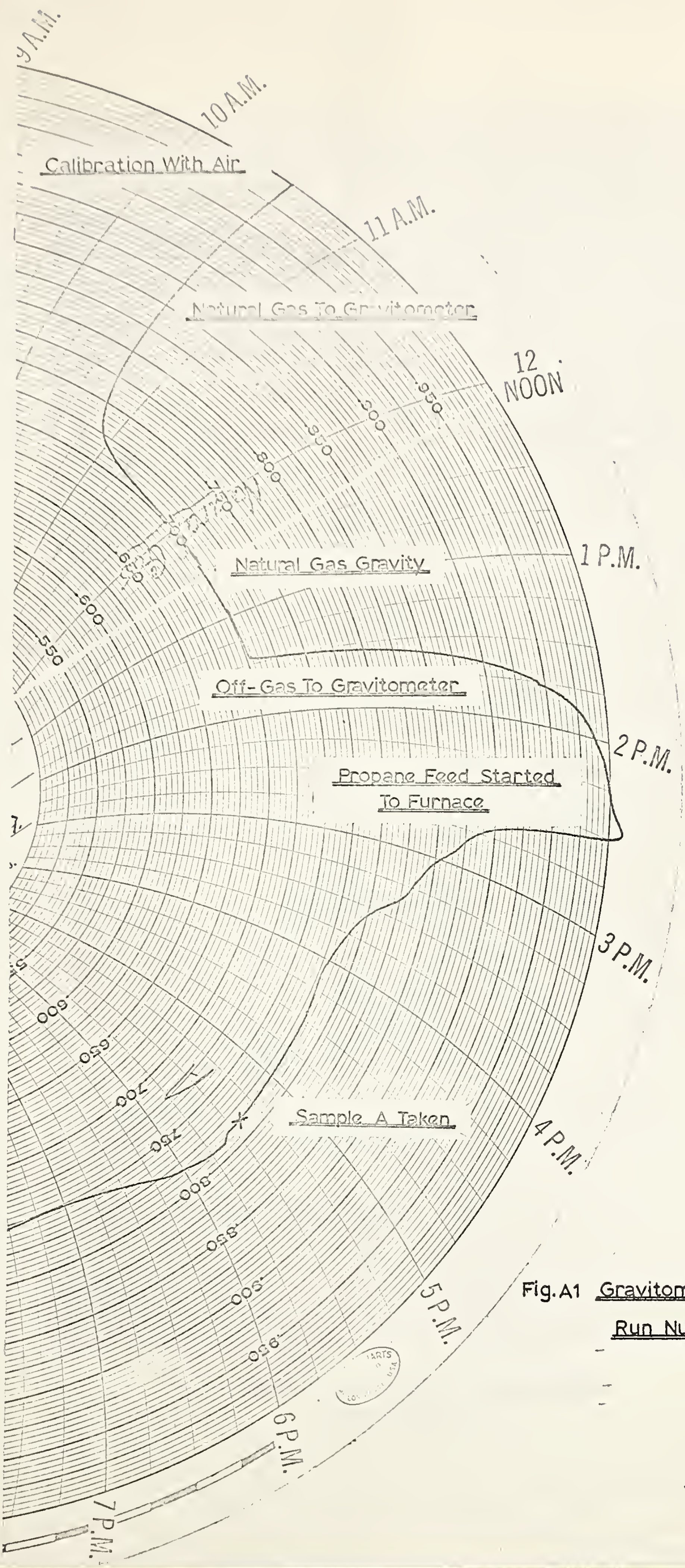


Fig. A1 Gravitometer Chart Run Number 11-A

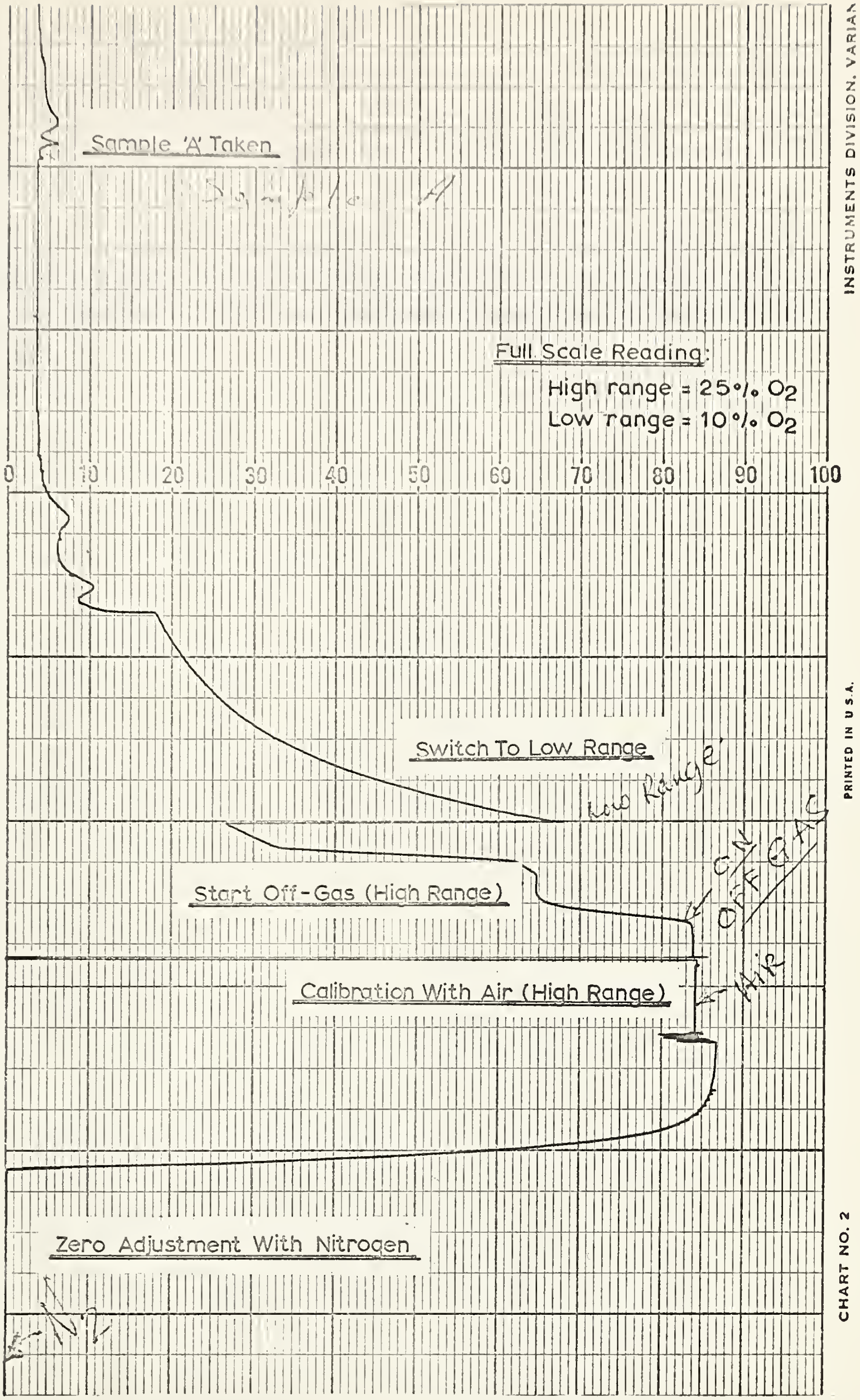
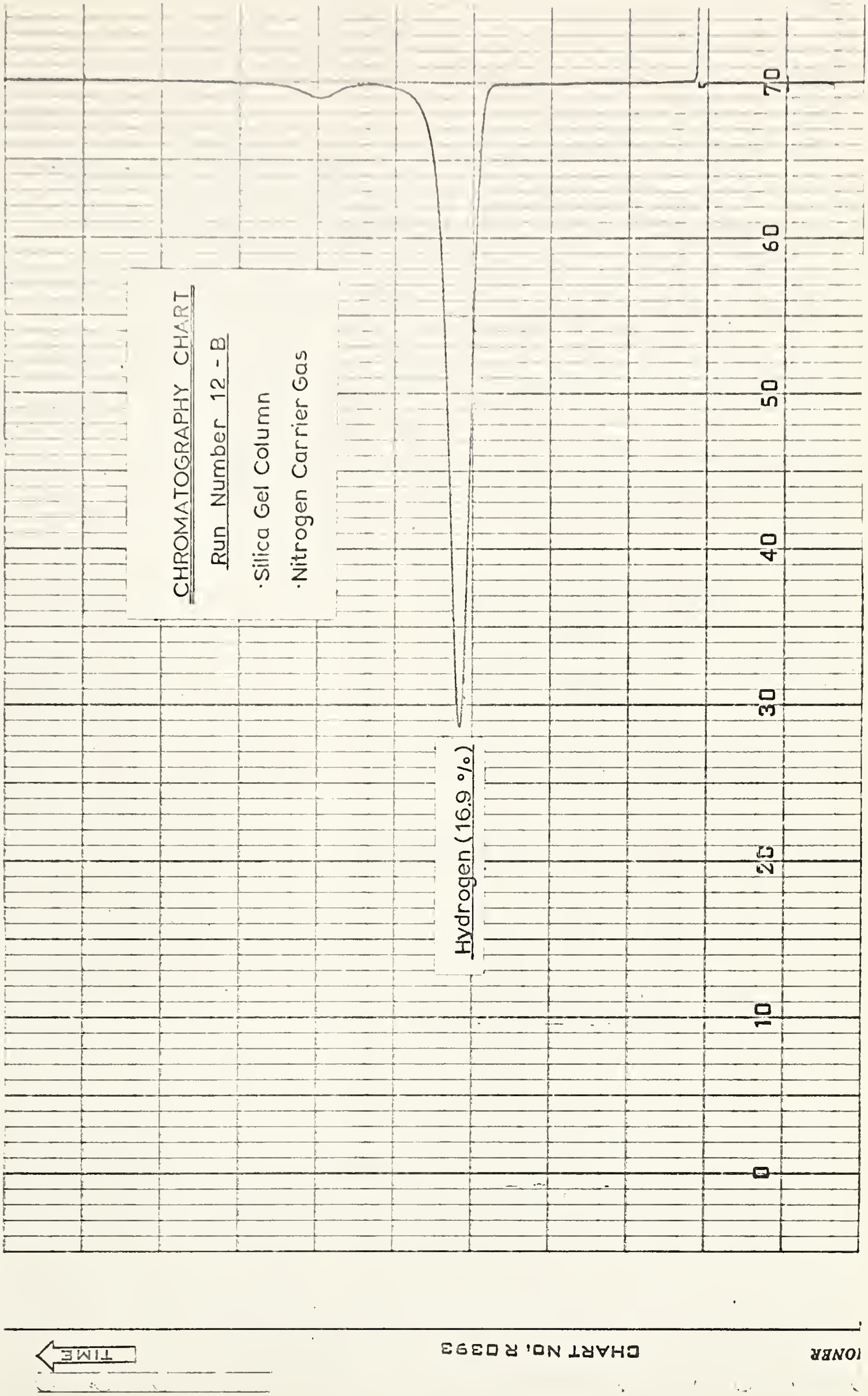


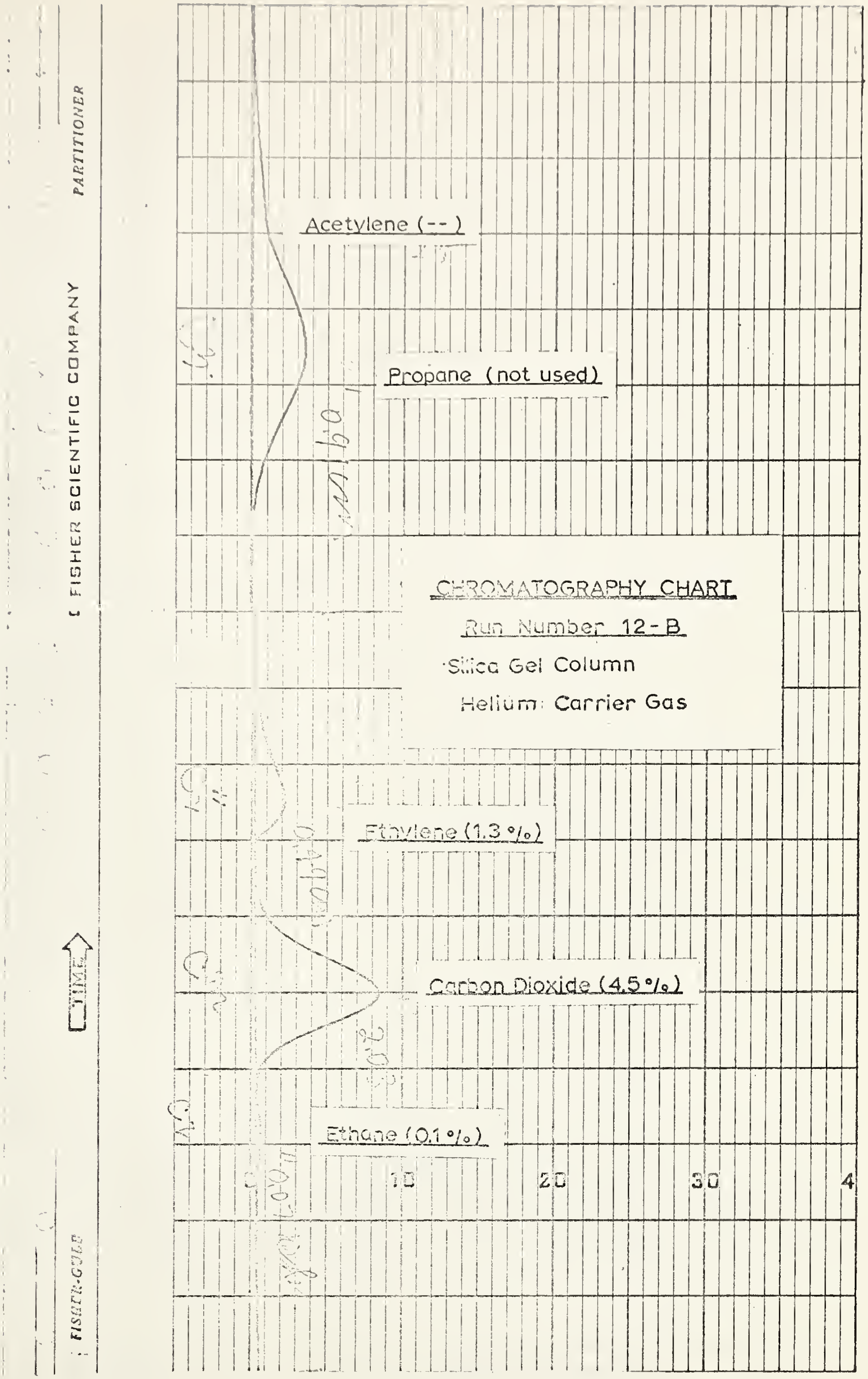
Fig. A2 Strip Chart From Oxygen Analyser

Run Number 11-A

APPENDIX "B"

Following are copies of strip charts from the gas chromatography unit. These charts are typical of the ones obtained during the analysis of the off-gas samples.


CHROMATOGRAPHY CHART
Run Number 12 - B
·Silica Gel Column
·Nitrogen Carrier Gas
Hydrogen (16.9 %)
0
10
20
30
40
50
60
70
CHART NO. R 0393
TIME

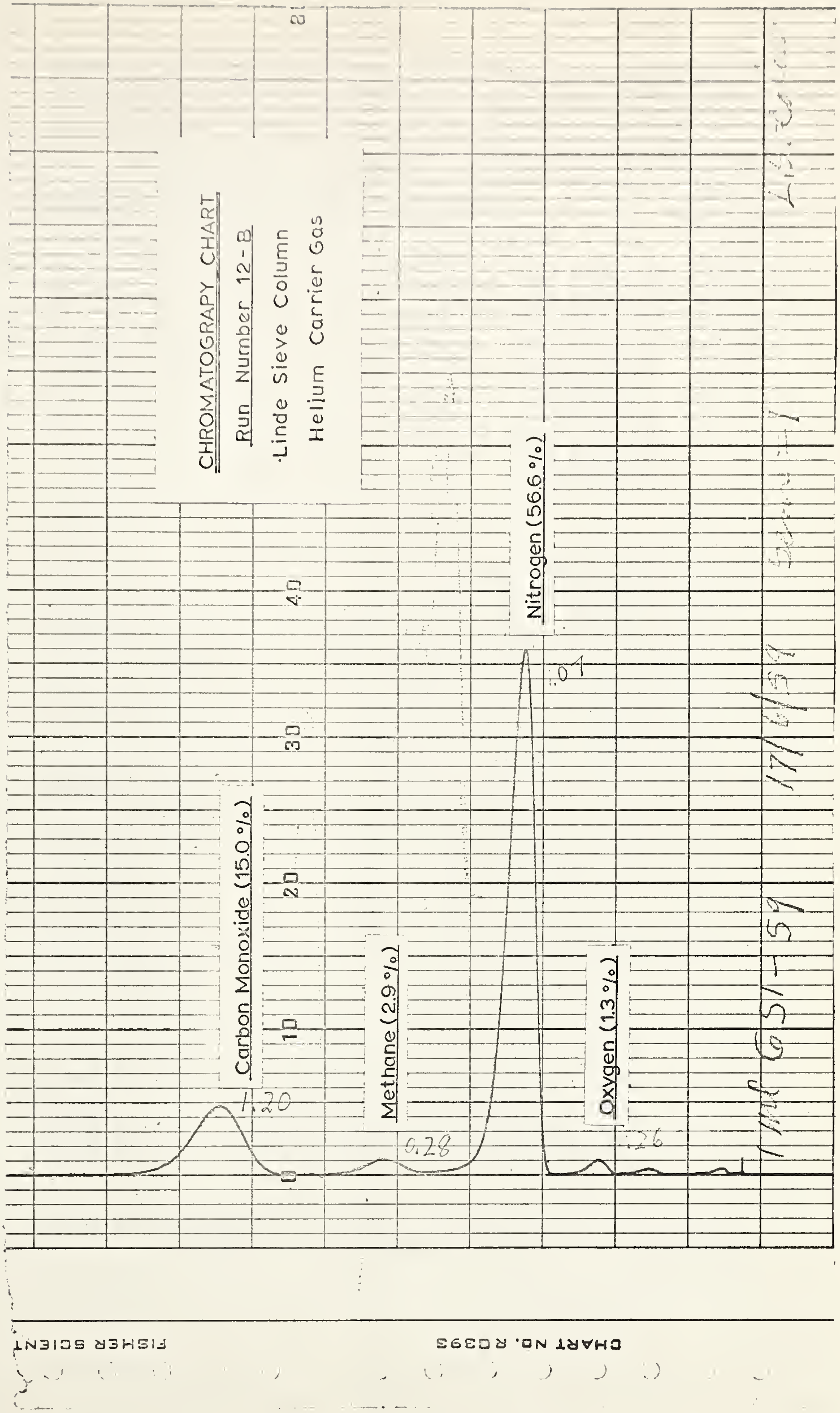


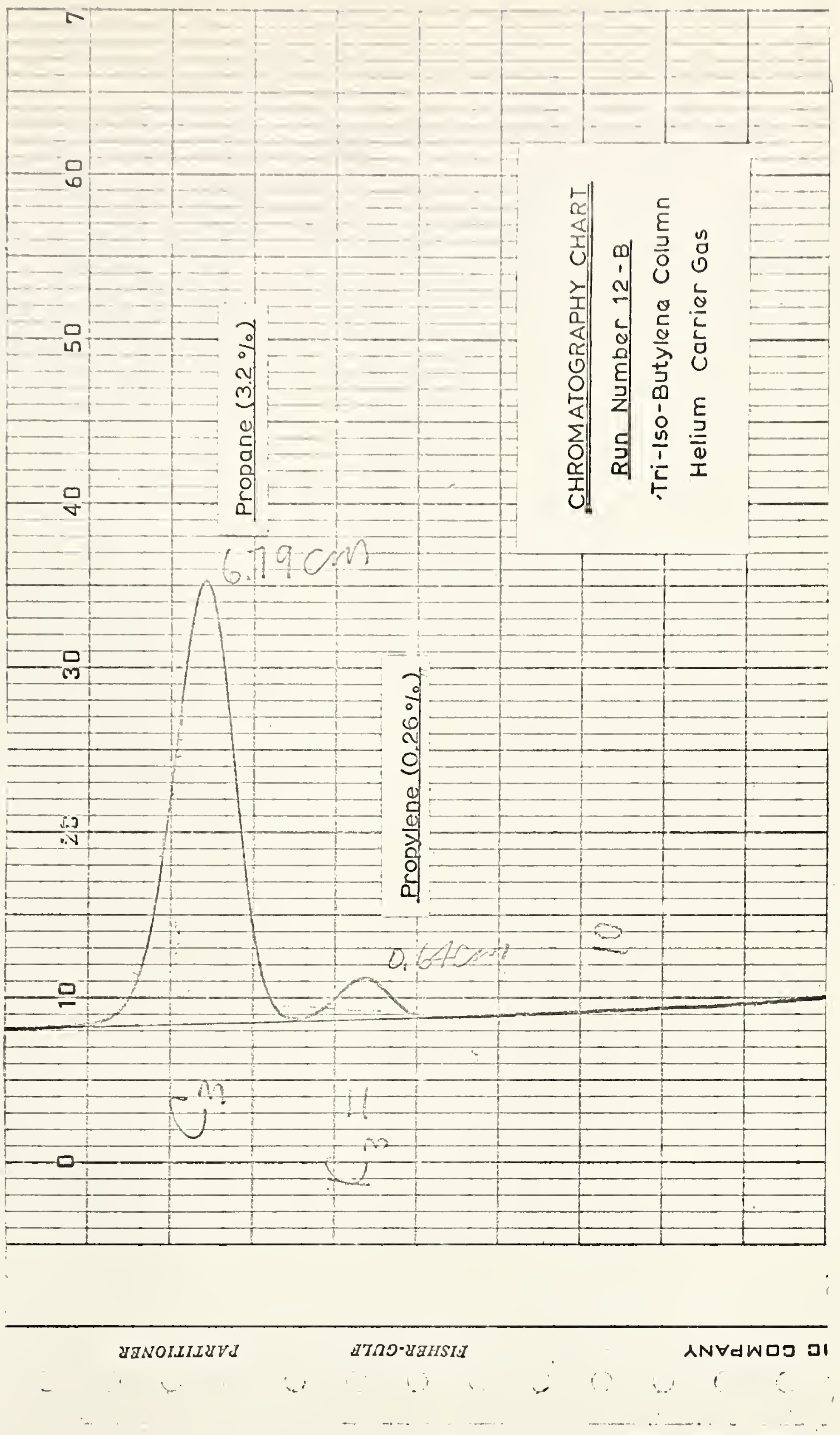
CHROMATOGRAPHY CHART

Run Number 12-B

Silica Gel Column

Helium Carrier Gas


CHROMATOGRAPY CHART
Run Number 12-B
Linde Sieve Column
Helium Carrier Gas
Carbon Monoxide (15.0 %)
Methane (2.9 %)
Nitrogen (56.6 %)
Oxygen (1.3 %)
1.20
0.28
.07
.26
0
10
20
30
40
80
1 ml 651-59
17/6/59
FISHER SCIENT
CHART NO. R0393


CHROMATOGRAPHY CHART
Run Number 12-B
Tri-Iso-Butylena Column
Helium Carrier Gas
Propane (3.2%)
6.79cm
Propylene (0.26%)
0.640cm
10
C_3
$C_3^=$
0
10
20
30
40
50
60
70
IC COMPANY
FISHER-GULF
PARTITIONER

B29800